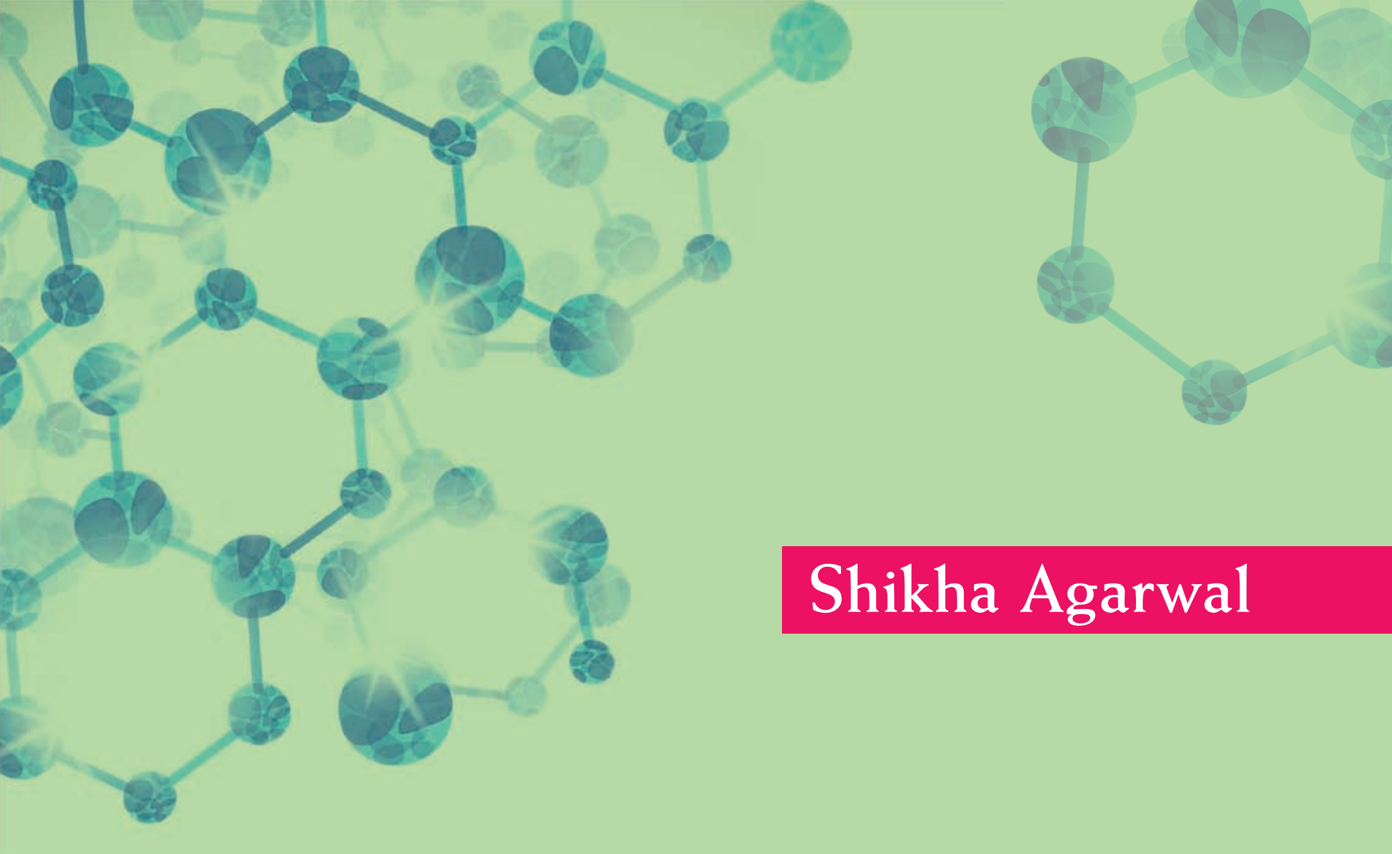

Shikha Agarwal

Engineering Chemistry

Fundamentals and Applications

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Dedicated to

His Holiness Shri Shivkripanand Swami

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Preface

Engineering chemistry is taught as a compulsory subject to first year undergraduate students of all the branches of engineering. The scope of the subject is very wide and writing a book for a heterogeneous variety of students across the country was a challenging assignment. The needs of the students are diversified and incorporate a combination of the both traditional topics and the latest trends in the subject including emerging areas like liquid crystals, green chemistry and nanochemistry.

This book has been organized to meet syllabi requirements of almost all Indian universities. The aim of this text is to enable the student to develop capabilities in self learning and understanding. It is a student oriented book and my teaching experience, stretching more than two decades, gave me insight into the mental status of the students at this level and the problems they confront while studying the subject. Two important facts have been kept in mind one, students reading this text are taking their first steps into the world of technical education and two, that English is a second language for most of these students.

Keeping these objectives in mind the book has been written in very simple language. The book has nearly 350 figures and illustrations, over 500 solved, unsolved problems along with review questions and it also includes more than 450 multiple choice questions.

All chapters are provided with highly descriptive and well labeled figures. A simple look at a figure will enable the student to grasp the underlying description. Theoretical explanations have been supplemented with solved and unsolved problems wherever required to enhance the process of understanding, learning and reproducing the principles involved. The problems have been blended with the text so that the student need not turn pages. The book aims to familiarize the student with the university pattern of examination: to meet this objective, numerical problems that have appeared in various university and board exams have been included at appropriate places.

Organization of the book

The book has been organized into twenty four chapters. It begins with topics of common interest like fuels, water, corrosion and phase rule followed by engineering materials, polymers and lubricants. The book then incorporates fundamental topics: structure and bonding, solid state, liquid crystals, chemical kinetics, surface chemistry, thermodynamics, electrochemistry, spectroscopy, photochemistry, fundamentals of organic chemistry, organometallic chemistry, green chemistry, nanochemistry, basics of environmental chemistry, chemical aspects of biotechnology, analytical techniques in chemistry, chemistry of compounds of carbon and hydrogen.

Chapter one 'Fuels' introduces the student to the basic definition of fuels, then proceeds to describe different types of fuels, their occurrence, purification, composition and uses. In addition it discusses the manufacture of fuels. The chapter also outlines renewable energy sources and their utility in the present scenario. *Chapter two* on 'Water' lays emphasis on the industrial end uses of water with special emphasis on hard water and its effects in industry. It deals with the principles involved in the softening of water like zeolite method, ion exchange method and it explains the latest techniques for desalination of brackish water by reverse osmosis and flash evaporation process. The chapter devotes a section to the analysis of hard water. Corrosion has a massive impact in industry and its study is of great significance for an engineering student. *Chapter three* underlines the causes, effects and measures to control corrosion. The latter half of this chapter lays special emphasis on corrosion control and outlines techniques like galvanizing, tinning, hot spraying, electroplating, electroless plating, organic coatings, etc. Similarly phase rule, engineering materials (cement, glass, refractories, abrasives and insulators), polymers are very important topics for the students at this level. These topics have been covered in *chapters four, five and six* respectively. The chapter on phase rule familiarizes the student with the fundamentals like what is a phase, what is a component, what are degrees of freedom, what is a phase diagram, difference between a true equilibrium and a metastable equilibrium and other fundamentals. To clarify these basic concepts, definitions are followed-up by plenty of examples. After ensuring that the student has grasped the basics, the chapter proceeds to explain the phase diagrams of various one component and two component systems and their applications. The second half of the chapter deals with metals and their alloys. This topic is important for understanding the behaviour of metals, their properties and variations in their properties depending on different phases and their composition. It explains advantages of alloys over pure metals and also explains the properties and uses of common alloys.

Chapter six on polymers not only explains fundamental concepts and basic definitions but also deals with the properties like glass transition temperature, viscoelasticity, anelasticity which are of immense industrial utility. The chapter explains various polymerization techniques like bulk polymerization, solution polymerization and suspension polymerization. Plastics and their manufacturing techniques like compression moulding, transfer moulding, blow moulding and extrusion moulding have been illustrated. Fibres and adhesives are also discussed. Apart from dealing with the preparation and uses of commonly known polymers the chapter lays special emphasis on speciality polymers like engineering thermoplastics, conducting polymers, electroluminescent polymers, liquid crystalline polymers like kevlar, biodegradable polymers and composite polymers like reinforced plastics.

Chapter seven 'Lubricants' explains the significance, properties and types of lubricants; their selection and suitability for different types of machinery. *Chapter eight* 'Structure and bonding' deals with the fundamental principles and various theories of bonding in molecules like valence bond theory, molecular orbital theory, band theory of solids. The chapter explains basic concepts like hybridization, overlap of orbitals, filling of electrons in the orbitals and also explains the dual nature of matter, de-Broglie relationship and Schrodinger wave equation. *Chapter nine* highlights the fundamentals of solid state. It explains fundamental concepts like unit cell, crystal lattice, packing of crystals, Braggs law and the structure of common crystals. To help the student visualize these structures, the chapter has plenty of figures. Moreover numerical problems to enhance understanding of crystals have been integrated into the text. *Chapter ten* gives an introductory idea about the fourth phase of matter – liquid crystals.

Chapters eleven, twelve, thirteen, fourteen and sixteen cover important topics in physical chemistry like chemical kinetics, surface chemistry, thermodynamics and photochemistry. Special care has been taken to illustrate the derivations step by step. Important relations and mathematical formulae have been provided in the summary of these topics. I am hopeful that the formulae given at the end will be very useful for students and instructors in understanding the basic concepts and theory of these topics.

Chapter fifteen deals with ultraviolet, infrared and NMR spectroscopy. It explains the fundamentals, basic instrumentation required for spectroscopy study in different regions and the application of spectroscopic techniques in chemistry.

Chapters seventeen concerns itself with are topics on organic chemistry. Fundamental organic concepts like inductive effect, resonance, hyperconjugation, electromeric effect, reaction intermediates like carbocation, carbonium ions, free radicals, nitrenes, carbenes have been discussed in sufficient details with lots of supporting examples. The chapter also discusses different types of organic reactions like addition, elimination, substitution and rearrangement reactions. Common name reactions alongwith their mechanism and applications have also been explained. Stereochemistry and its basic concepts have also been dealt. Organometallic compounds and their applications have been discussed in *chapter eighteen*.

To promote the concept of sustainable development green chemistry is gaining importance. The twelve principles of green chemistry and its applications are explained in *chapter nineteen*. *Chapter twenty* deals with nanochemistry. It gives an introductory idea to fundamentals like Top-Down and Bottom-Up approaches to nanoparticles. Important nanomaterials like carbon nanotube, nanowires, nanocones and haeckalites have been discussed in brief along with their applications. Fundamentals of environment science, pollution control, solid waste management and major environmental issues like acid rain, ozone depletion, wetland depletion, deforestation, biodiversity, soil erosion have been explained in sufficient detail in *chapter twenty on*e. Biotechnology is the application of technology to living organisms to modify products or processes for specific use. An introduction to the basic principles and their applications has been dealt with in *chapter twenty two*.

The use of highly sophisticated instruments in science has made analysis accurate. *Chapter twenty three* introduces the student to various analytical techniques in chemistry. The text ends with a discussion on the chemistry of carbon and hydrogen in the *last chapter*.

Throughout the text I have tried to maintain simplicity of language. Unnecessary details have been omitted and the book contains only as much material as is required for the target students. I hope it will serve its purpose and both teachers and students in various streams will benefit. I look forward to suggestions from esteemed faculty members and students, as their inputs will invariably help me to improve the book in future. Although great care has been taken to make the book as error free as possible but *to err is human;* I extend apologies for errors left inadvertently in the text and also look forward to suggestions from my friends and colleagues from the teaching fraternity across the country.

Acknowledgments

"*To speak gratitude is courteous and pleasant, to enact gratitude is generous and noble, but to live gratitude is to touch heaven*"

A project of this dimension could not be completed without the support, advice and suggestions of colleagues, friends and family members. It is my divine duty to acknowledge the contribution of every person whose effort has made this project see the light of the day. I bow my head in reverence to my spiritual Guru and the almighty God for giving me the internal strength and self discipline for this assignment. I take this opportunity to thank the reviewers for their valuable suggestions for the book. Topics like Battery Technology and Nanochemistry have been added and Cement, Glass, Refractories were placed together under Engineering Materials on the valuable advice of the reviewers selected by the publisher. I extend sincere thanks to Professor C. P. Sharma (MNIT, Jaipur), Professor K. D. Gupta (MNIT, Jaipur), Dr Dinesh Gupta (Member Secretary, RPSC) and Dr P. C. Jain (Retd Professor GCA), Dr Shashi Chawla (Amity University) for their scholarly advice. I owe sincere gratitude to Dr M. M. Sharma (Principal, Government Engineering College, Ajmer) for providing a positive work environment. I am also grateful to my friends and colleagues Dr Deepika Sharma, Dr Sangeeta Krishnan, Dr Pooja Tomar and Dr Suresh Sahu for their valuable suggestions. My family deserves a special mention. My husband Harsh Gupta stood behind me as a pillar of strength. Inspite of his extremely busy schedule he found time to prepare the initial typescript of this work. In fact this work, at my end, owes its timely completion to him. My daughter Surabhi, a student of class twelfth, provided me a student's eye-view of the script and not to forget little Kanishka whose bed time stories were sacrificed at the altar of this work.

In the end I express my gratitude to the editorial team at Cambridge: Gauravjeet Singh Reen (Commissioning Editor) for his excellent ground work and syllabus research that helped me in deciding the table of contents. I always turned to him for suggestions wherever I was stuck and he was always available to answer my queries. Members of the academic editorial team Hardip Grewal (Editorial Consultant, Science) and Shikha Vats (Assistant Production Manager) were also very cooperative and gave me advice and suggestions as and when required.

Last but not the least I am thankful to all my students and teachers who have taught me and made me what I am today.

Chapter 1

FUELS

1.1 Introduction

A fuel is a substance that produces useful energy either through combustion or through nuclear reaction. An important property of a fuel is that the energy is released in a controlled manner and can be harnessed economically for domestic and industrial purposes. Wood, coal, charcoal, petrol, diesel, kerosene, producer gas and oil gas are some of the common examples of fuels.

Fuels that produce heat energy by combustion are termed as *chemical fuels*. During combustion, carbon, hydrogen, sulphur and phosphorus that are present in the fuel combine with oxygen and release energy.

$$\text{Fuel} + O_2 \rightarrow \text{Products} + \text{Heat}$$

$$C + O_2 \rightarrow CO_2 + \text{Heat}$$

$$2H_2 + O_2 \rightarrow 2H_2O + \text{Heat}$$

However, combustion is not always necessary for a fuel to produce heat. Energy can also be liberated by fission or fusion of nuclei. This energy is much greater than the energy released by chemical fuels, and such fuels are termed as *nuclear fuels*. For example, plutonium, tritium, uranium, etc.

1.2 Classification of Fuels

Fuels can be classified on the basis of their (I) Occurrence (II) Physical State

(I) On the basis of occurrence, fuels are of two types

(a) **Primary Fuels or Natural Fuels** These are found to occur in nature and are used as such either without processing or after being processed to a certain extent, which does not alter the chemical constitution of the fuel. These are also known as fossil fuels. Examples include wood, peat, lignite, coal, petroleum, natural gas, etc.

(b) **Secondary Fuels or Derived Fuels** These are the fuels that are derived from primary fuels by further chemical processing; for example, coke, charcoal, kerosene, producer gas, water gas, etc

(II) On the basis of their physical state, fuels may be classified as follows

(a) Solid fuels

(b) Liquid fuels

(c) Gaseous fuels

The classification can be summarized as

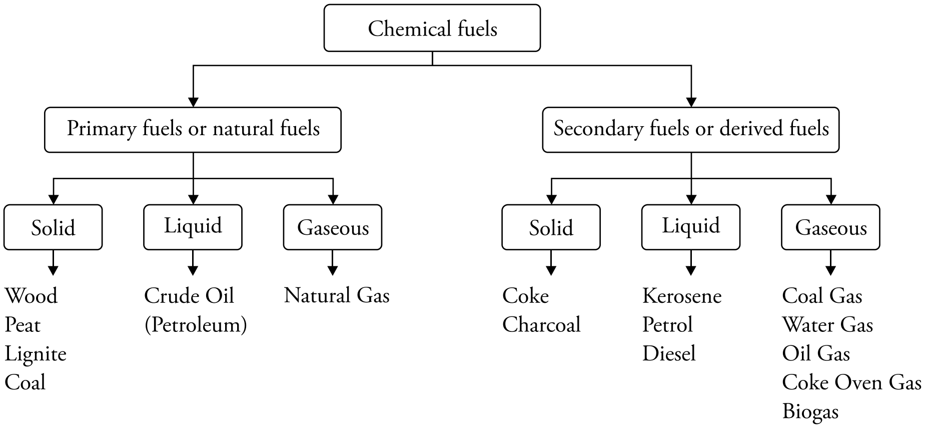

Figure 1.1 *Classification of fuel*

1.3 Characteristics of a Good Fuel

1. ***High Calorific value*** A good fuel should possess high calorific value because calorific value determines the efficiency of the fuel. Higher the calorific value greater is the heat liberated per unit mass or volume.
2. ***Ignition Temperature*** It is the lowest temperature to which a fuel must be preheated so that it starts burning smoothly. An ideal fuel should have moderate ignition temperature. Low ignition temperature can cause fire hazards, making storage and transportation difficult. Fuel with low ignition temperature can burn spontaneously leading to explosion. High ignition temperature, on the other hand, makes it difficult to kindle (ignite) the fuel.
3. ***Moisture Content*** Moisture content should be low because the presence of moisture lowers the calorific value of the fuel.

4. ***Non–combustible matter*** After combustion, the non-combustible matter is left behind as ash or clinkers. Non-combustible matter reduces the calorific value of the fuel and also requires additional money investment for storage, handling and disposal of the waste products produced.
5. ***Velocity of combustion*** If the velocity of combustion is low, then a part of the liberated heat may get radiated instead of raising the temperature; hence, the required high temperature may not be attained. On the other hand, if the velocity of combustion is very high then the rate of combustion might become uncontrollable. For a continuous supply of heat, fuel must burn with a moderate rate.
6. ***Combustion products*** The products obtained during combustion of the fuel should be harmless and non-polluting. Harmful gases such as CO_2, SO_2, H_2S, PH_3 and $PbBr_2$ should not be produced, and also the amount of smoke produced should be less.
7. ***Cost of the fuel*** A good fuel should be readily available at a low cost.
8. ***Storage and transportation*** A good fuel should be easy to handle, store and transport at low cost.
9. ***Size*** In case of solid fuels, the size should be uniform so that combustion is regular.
10. ***Combustion should be controllable*** The combustion process should be controllable, i.e., it can be started or stopped when required.

Table 1.1 Comparison of solid, liquid and gaseous fuel

S.No.	Solid Fuel	Liquid Fuel	Gaseous Fuel
1	Cheap and easily available.	Costlier than solid fuel except in the countries of origin.	Costly, because except natural gas all other gaseous fuels are derived from solid and liquid fuels.
2	Convenient to store without any risk of spontaneous explosion.	Great care must to be taken to store them in closed containers.	Very large storage tanks are needed. Storing gaseous fuel requires extra care as they are highly inflammable.
3	Large space is required.	Storage space is less compared with solid and gaseous fuels.	They must be stored in leak proof containers.
4	They are easy to transport.	They can be easily transported through pipelines.	They can also be transported through pipelines.
5	They posses moderate ignition temperature. Combustion is slow but it cannot be controlled easily.	Combustion takes place readily and can easily be controlled or stopped by reducing or stopping the fuel supply.	Combustion is fast and can be controlled and stopped easily.
6	Ash is produced and its disposal is a big problem. Smoke is also produced.	Ash is not produced, however fuels with high carbon and aromatic contents may produce smoke.	Neither ash nor smoke is produced.
7	They cannot be used in internal combustion engine.	Used in internal combustion engine (petrol, diesel).	Used in internal combustion engines (CNG,LPG)

8	They have low thermal efficiency.	Their thermal efficiency is higher than solid fuels.	Their thermal efficiency is highest.
9	Their calorific value is lowest.	Their calorific value is higher than solid fuels.	Their calorific value is the highest.
10	Least risk of fire hazards.	Risk of fire hazards is high.	Highest risk of fire hazards.

1.4 Calorific Value

It is defined as the total amount of heat liberated when a unit mass or volume of fuel is burnt completely.

Units of heat

(i) ***Calorie*** It is defined as the amount of heat required to raise the temperature of 1 g of water by 1°C (from 15°C to 16°C)

1 Calorie = 4.185 Joules = 4.185×10^7 Ergs.

(ii) ***Kilocalorie*** It is defined as the amount of heat required to raise the temperature of 1 kg of water by 1°C (from 15°C to 16°C). 1 Kcal = 1000 Cal

(iii) ***British Thermal Unit*** (*B.T.U*). It is defined as the amount of heat required to raise the temperature of 1 Pound (lb) of water by 1 °F (from 60° F to 61° F)

1 B.T.U = 252 Cal = 0.252 Kcal = 1054.6 Joule = 1054.6×10^7 Ergs.

(iv) ***Centigrade Heat Unit*** (*C.H.U*). It is defined as the amount of heat required to raise the temperature of one pound of water by 1°C (from 15°C to 16°C).

1 Kcal = 3.968 B.T.U. = 2.2 C.H.U.

Units of calorific value

The units of calorific value for solid, liquid and gaseous fuels are given below.

System	Solid / Liquid fuels	Gaseous fuels
CGS	calories/gm	calories/ cm^3
MKS	Kcal/Kg	Kcal/m^3
BTU	B.T.U./lb	B.T.U./ ft^3

These units can be interconverted as follows

1 cal/g =1 Kcal/kg = 1.8 B.T.U./lb

1 Kcal = 0.1077 B.T.U./ft^3

1 B.T.U. /ft^3 = 9.3 Kcal/m^3.

Gross and Net Calorific Value

***Gross Calorific Value* (*GCV*)** It is also called higher calorific value (HCV) and is defined as the total amount of heat produced when a unit quantity (mass/volume) of fuel is burnt completely, and the products of combustion are cooled to room temperature.

Usually all fuels contain hydrogen. During combustion, the hydrogen present in the fuel is converted into steam. When the combustion products are cooled to room temperature, the steam gets condensed into water and heat that equals the latent heat of condensation of steam is evolved. This heat gets included in the measured heat, and so its value is high; hence, it is called higher calorific value.

***Low Calorific Value* (*LCV*)** It is also termed as net calorific value (NCV) and is defined as the heat produced when a unit quantity (mass/volume) of a fuel is burnt completely and the hot combustion products are allowed to escape.

In actual practice, when a fuel is burnt water vapor escapes along with the hot combustion gases; hence, heat available is lesser than the gross calorific value. Therefore, this is called low calorific value (LCV) or net calorific value (NCV).

Thus LCV = HCV – Latent heat of water vapour formed.

As 1 part by weight of hydrogen gives 9 parts by weight of water,

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O$$

LCV = HCV – Weight of hydrogen in fuel × 9 × latent heat of steam

Solved Examples

1. 2 kg of a coal sample was burnt in a bomb calorimeter. The heat liberated was estimated and found to be 14114 Kcal. Calculate the calorific value of the coal sample.

Solution

Heat liberated on burning 2 Kg coal = 14114 Kcal.

Therefore, heat liberated on combustion of 1 Kg coal = $\frac{14114}{2} = 7057 \text{ Kcal}$.

[Ans Calorific value of coal = 7057 Kcal/kg].

2. The gross calorific value of a fuel containing 8% hydrogen was found to be 9225.9 Kcal/kg. Find out its net calorific value if the latent heat of steam is 587 Kcal/kg.

Solution

$$\begin{aligned} \text{NCV} &= \text{GCV} - 0.09\,\text{H} \times \text{Latent heat of steam.} \\ \text{NCV} &= 9225.9 - 0.09 \times 8 \times 587. \\ &= 9225.9 - 422.64 = 8803.26 \text{ Kcal/kg} \end{aligned}$$

[Ans LCV/NCV = 8803.26 Kcal/kg].

Practice problems

1. Calculate the GCV of a coal sample if its LCV is 6767.45 cal/g and if it contains 5% hydrogen. (Latent heat of steam is 587 cal/g).

   [Ans GCV = 7031.6 cal/g].

2. The gross calorific value of a fuel containing 6% H was found to be 9804.6 Kcal/kg. Find the net calorific value if the latent heat of steam is 587 cal/g.

   [Ans 9487.62 Kcal/Kg].

Determination of Calorific Value

The calorific value of solid and non-volatile liquid fuels is determined by Bomb Calorimeter, whereas the calorific value of gaseous fuels is determined by Junkers Calorimeter.

Bomb calorimeter

Principle A known amount of fuel is burnt in excess of oxygen and the heat liberated is absorbed in a known amount of water. This heat liberated is measured by noting the change in temperature. Calorific value of the fuel is then calculated by applying the following principle

Heat liberated by fuel = Heat absorbed by water and the calorimeter.

Construction A simple sketch of the bomb calorimeter is shown in the Fig. 1.2 given below.

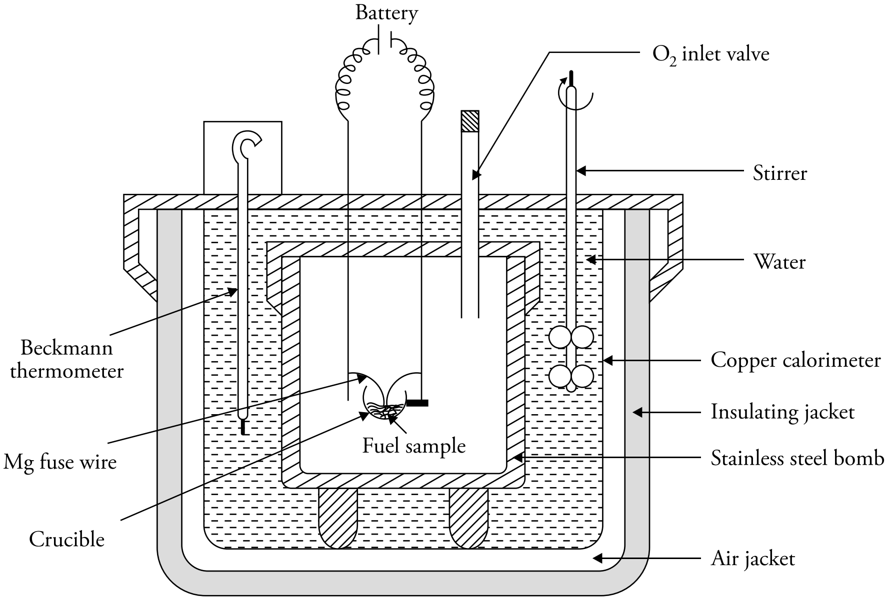

Figure 1.2 *Bomb calorimeter*

It consists of the following parts

(i) ***Stainless steel bomb*** It consists of a long cylindrical container made up of stainless steel. It has a lid that is made air tight with the help of screws. The lid is provided with two holes for electrodes and has an oxygen inlet valve. A small ring is attached to one of the electrodes. This ring acts as a support for nickel or stainless steel crucible in which the fuel is burnt. Magnesium wire touching the fuel sample extends across the electrodes. The steel bomb is lined inside with platinum to resist corrosive action of HNO_3 and H_2SO_4 vapors formed because of burning of fuel and is designed to withstand high pressure (25–50 atm).

(ii) ***Copper calorimeter*** The bomb is placed in a copper calorimeter containing a known amount of water. The calorimeter is provided with an electrical stirrer and a Beckmann thermometer that can read accurate temperature difference of up to 1/100th of a degree.

(iii) ***Air jacket and water jacket*** The copper calorimeter is surrounded by an air jacket and a water jacket to prevent loss of heat owing to radiation.

Working A known amount of fuel (0.5–1 g) is taken in a clean crucible supported over the ring. A fine magnesium wire, touching the fuel sample, is then stretched across the electrodes. About 10 ml of distilled water is introduced into the bomb to absorb vapors of sulphuric acid and nitric acid formed during combustion, and the lid of the bomb is tightly screwed. The bomb is filled with oxygen at 25 atmospheric pressure and placed in the copper calorimeter containing a known weight of water. The stirrer is started and the initial temperature of water is noted. The electrodes are then connected to a 6-volt battery to complete the circuit. The sample burns and heat is liberated. This heat is absorbed by water. Maximum temperature shown by the thermometer is recorded. Time taken to cool the water in the calorimeter from maximum temperature to room temperature is also noted. The gross calorific value of the fuel is calculated as follows.

Calculations

Let,
Weight of fuel sample taken = x gm.
Weight of water in the calorimeter = W gm.
Water equivalent of calorimeter,
stirrer, thermometer, bomb etc = w gm.
Initial temperature of water in the calorimeter = t_1°C.
Final temperature of water in the calorimeter = t_2°C.
Higher calorific value of fuel = H calorie / gm.
Heat liberated by burning of fuel = $x \times H$.
Heat gained by water = $W \times \Delta T \times$ specific heat of water.
= $W(t_2 - t_1) \times 1$ cal.
Heat gained by calorimeter = $w(t_2 - t_1)$.
Total heat gained = $W(t_2 - t_1) + w(t_2 - t_1)$.
= $(W + w)(t_2 - t_1)$.

But,
Heat liberated by the fuel = Heat absorbed by water and calorimeter.

$$x \times H = (W + w)(t_2 - t_1)$$

$$H = \frac{(W+w)(t_2-t_1)}{x} \text{ cal/gm (or Kcal/Kg)}$$

Net (lower) calorific value
LCV = HCV – 0.09H × 587 cal/gm or Kcal/Kg
(Latent heat of condensation of steam = 587 Kcal/Kg)

Corrections

Following corrections are applied to get more accurate results

(a) ***Fuse wire correction*** The gross calorific value calculated above includes the heat liberated by the ignition of Mg fuse wire; hence, this amount of heat has to be subtracted from the total value.

(b) ***Acid Correction*** During combustion, sulphur and nitrogen present in the fuel get oxidized to H_2SO_4 and HNO_3, respectively

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad \Delta H = -144000 \text{ cal}$$

$$2N_2 + 5O_2 + 2H_2O \rightarrow 4HNO_3 \qquad \Delta H = -57160 \text{ cal}$$

Hence, the formation of acids is exothermic and this should be subtracted from the obtained value of GCV.

(c) ***Cooling Correction*** Heating and cooling are simultaneous processes. As the temperature rises above the room temperature, the loss of heat occurs due to radiation and the highest temperature recorded will be slightly less than that obtained if there was no heat loss. A temperature correction (cooling correction) is therefore necessary to get the correct rise in temperature.

If the time taken for the water in the calorimeter to cool from maximum temperature attained to room temperature is '*x*' minutes and the rate of cooling is dt / min, then the cooling correction is *x* × dt and this is to be added to the rise in temperature.

$$\text{HCV of fuel (H)} = \frac{(W+w)(t_2-t_1+\text{cooling correction})-(\text{Acid + fuse wire correction})}{\text{Mass of the fuel}(x)}$$

Solved examples

1. 0.72 g of a fuel containing 80% carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3°C to 29.1°C. If the calorimeter contains 250 g of water and its water equivalent is 150 g, calculate the HCV of the fuel. Give your answer in kJ/Kg.

Solution

Here $x = 0.72$ g, W = 250 g, w = 150 g, $t_1 = 27.3°C$, $t_2 = 29.1°C$

Therefore, HCV of fuel $(\mathrm{H}) = \frac{(W+w)(t_2-t_1)}{x}$ cal/g

$\frac{(250+150)(29.1-27.3)}{0.72}$ cal/g = 1000 × 4.18 J/g = 4180 J/g = 4180. KJ/Kg

(1 cal = 4.18 Joules).

2. On burning 0.83 g of a solid fuel in a bomb calorimeter, the temperature of 3500 g of water increased from 26.5°C to 29.2°C. Water equivalent of calorimeter and latent heat of steam are 385.0 g and 587.0 cal/g respectively. If the fuel contains 0.7% hydrogen, calculate its gross and net calorific values.

Solution

Here, Weight of fuel (x) =0.83 g; weight of water (W) = 3500 g; water equivalent of calorimeter (w) = 385 g; $(t_2 - t_1)$ = (29.2°C – 26.5°C) = 2.7°C; percentage of hydrogen (H) = 0.7%; Latent heat of steam = 587 cal/g.

HCV of fuel (H) $= \frac{(W+w)(t_2-t_1)}{x}$ cal/g $= \frac{(3500+385)\times 2.7}{0.83} = 12{,}638$ cal/g

Net calorific value = (HCV – 0.09 H × 587) = (12638 – 0.09 × 0.7 × 587)cal/g.

= (12,638–37) cal/g = 12,601 cal/g

3. A coal sample contains : C = 93%; H = 6% and ash = 1%. The following data were obtained when the above coal was tested in a bomb calorimeter :
   (i) Wt of coal burnt = 0.92 g
   (ii) Wt of water taken = 550 g
   (iii) Water equivalent of bomb and calorimeter = 2200 g
   (iv) Rise in temperature = 2.42°C
   (v) Fuse wire correction = 10.0 cal
   (vi) Acid correction = 50.0 cal

   Calculate the gross calorific value of the coal.

   Solution

   Wt of coal (x) = 0.92 g; Wt of water taken (W) = 550 g

   Water equivalent of bomb and calorimeter (w) = 2200 g

   Rise in temperature $(t_2 – t_1)$ = 2.42°C; Fuse wire correction =10.0 cal

Acid correction =50.0 cal; latent heat of condensation of steam = 580 cal/g;
Percentage of hydrogen = 6%

$$\text{GCV} = \frac{(W+w)(t_2-t_1)-(\text{Acid + fuse wire correction})}{x}$$

$$= \frac{(550+2200)\times 2.42\times(50+10)}{0.92} = 7168.5 \text{ cal/g}$$

4. A coal sample contains C = 92%; H = 5% and ash = 3%. When this coal sample was tested in the laboratory for its calorific value in a bomb calorimeter, the following data were obtained
   Wt of coal burnt = 0.95 g
   Wt of water taken = 700 g
   Water equivalent of bomb and calorimeter = 2000 g
   Rise in temperature = 2.48°C
   Fuse wire correction = 10.0 cal
   Acid correction = 60.0 cal
   Cooling correction = 0.02°C

   Calculate the gross and net calorific value of the coal sample in cal/g. Assume the latent heat of condensation of steam as 580 cal/g.

Solution

$$\text{GCV} = \frac{(W+w)(t_2-t_1+\text{cooling correction})-(\text{acid correction + fuse wire correction})}{\text{weight of coal sample taken}}$$

$$= \frac{(2000+700)(2.48+0.02)-(10+60)}{0.95} = \frac{(2700)(2.50)-(70)}{0.95}$$

$$= \frac{6750-70}{0.95} = \frac{6680}{0.95} = 7031.57 \text{ cal/g}$$

LCV or NCV = HCV – 0.09H × 580 cal/g

= 7031.570 – 0.09 × 5 × 580

= 7031.57 – 261 = 6770.57 cal/g

[Ans HCV/GCV = 7031.57 cal/g

LCV/NCV = 6770.57 cal/g]

Practice problems

1. The temperature of 950.0 g of water was increased from 25.5°C to 28.5°C on burning 0.75 g of a solid fuel in a bomb calorimeter. Water equivalent of calorimeter and latent heat of steam are 400.0 g and 587.0 cal/g, respectively. If the fuel contains 0.65% of hydrogen, calculate its net calorific value.

   [Ans 5365.66 cal/g]

2. Liquid fuel weighing 0.98 g and containing 90.1% C, 8% H and having the following results in bomb calorimeter experiment

   Amount of water taken in calorimeter = 1450 g

   Water equivalent of calorimeter = 450 g

   Rise in temperature of water = 1.8°C

   If the latent heat of steam is 587 cal/g, calculate gross and net calorific value of fuel.

   [Ans GCV = 3489.79 cal/g; LCV = 3067.15 cal/g].

Calorific Value of Gaseous Fuels

Junker's Gas Calorimeter It is used for measuring the calorific value of gaseous and volatile liquid fuels.

Principle A known volume of gas is burnt at known pressure in a small enclosed combustion chamber. The heat liberated is absorbed by water flowing at constant rate through the water jacket. By knowing the initial and final temperatures of water, the quantity of water and weight of water condensed, the calorific value can be determined.

Construction

It consists of the following parts

1. ***Bunsen burner*** It is used for the combustion of gaseous fuel. It is clamped at the bottom and can be pulled out or pushed into the chamber during combustion.
2. ***Gasometer*** It measures the volume of the gas burning per unit time. It is attached with a manometer fitted with a thermometer to record the pressure and temperature of the gas before burning.
3. ***Pressure governor*** It regulates the supply of a gaseous fuel at constant pressure.
4. ***Gas calorimeter*** It consists of a vertical cylindrical combustion chamber where combustion of gaseous fuel is carried out. The combustion chamber is surrounded by an annular water space where water is made to circulate. Loss of heat by radiation and convection is prevented by an outer jacket, which is chromium-plated. Moreover, the outer jacket contains air that is a very good heat insulator. There are openings at appropriate places where thermometers are placed for measuring the temperature of the inlet and outlet water.

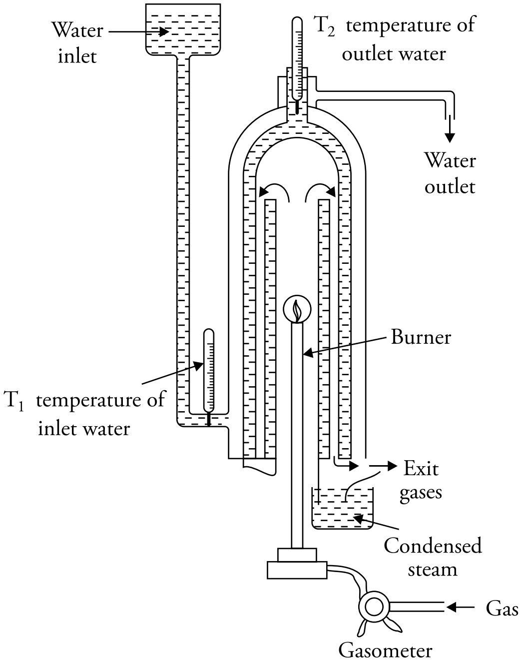

Figure 1.3 *Junker's gas calorimeter*

Working A known volume of gas is burnt at a constant rate in a combustion chamber in the presence of excess air. All the heat produced is absorbed by water circulating in the annular space around the combustion chamber.

Observations

(i) The volume of gaseous fuel burnt at a given temperature and pressure in a certain time = V m^3

(ii) Weight of water circulated through the coils in time t = W gm

(iii) Temperature of inlet water = t_1°C

(iv) Temperature of outlet water = t_2°C

(v) Weight of steam condensed in time t in a graduated cylinder = m kg.

Let Gross Calorific Value of the fuel = H
Heat produced by the combustion of fuel = V × H
Heat absorbed by circulating water = $W (t_2 - t_1)$

Assuming no loss of heat

$$V \times H = W (t_2 - t_1)$$

HCV or GCV

$$H = \frac{W(t_2 - t_1)}{V} \text{ Kcal/m}^3$$

Weight of steam condensed in a certain time *t* by the combustion of V m^3 of the fuel = m Kg
Mass of H_2O condensed per m^3 of the fuel = m/V kg

$$\text{As latent heat of steam per m}^3 \text{ of the fuel} = \frac{m \times 587}{V} \text{ Kcal},$$

$$\text{therefore, NCV or LCV} = \left[H - \frac{m \times 587}{V}\right] \text{Kcal/m}^3$$

Boy's gas calorimeter

Like Junker's calorimeter, the Boy's gas calorimeter is also used to find the calorific value of gaseous and volatile liquid fuels. It consists of the following parts

1. **Gas Burner** Gas burner is used for the combustion of a known volume of gas at a known pressure. The volume of the gas burnt is measured with the help of a gasometer and the pressure of the gas is monitored using pressure governor.
2. **Combustion Chamber** The combustion chamber or chimney having copper tubes coiled inside and outside the combustion chamber. Water circulates in these coils. It enters from the top of the outer coil, passes through the outer coils, moves to the bottom of the chimney and then moves upwards through the inner coil and exits from the top.

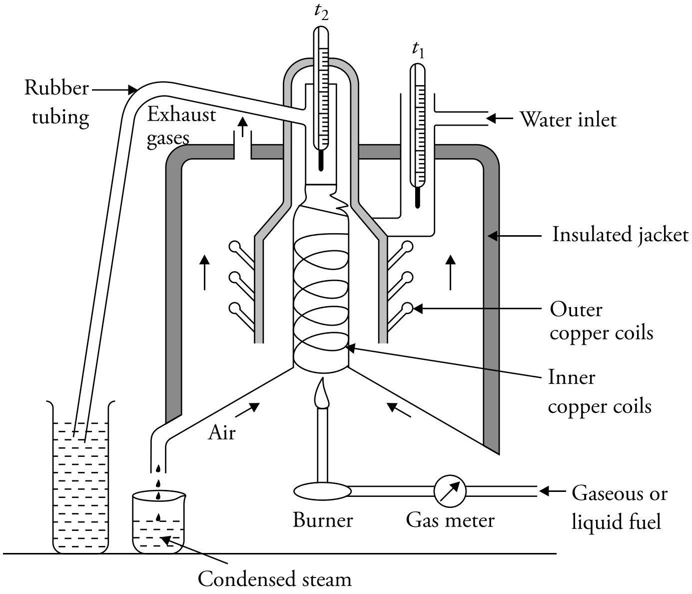

Figure 1.4 *Boy's gas calorimeter*

3. **Thermometers** Two thermometers t_1 and t_2 measure the temperatures of the incoming and outgoing water.
4. A graduated beaker is placed at the bottom to collect the condensed steam produced during combustion.

Working The working is similar to Junker's calorimeter. The water is circulated and the fuel is burnt to provide an initial warming period of 15 minutes. When the calorimeter is warmed, the rate of flow of the gas is adjusted and it is burnt inside the calorimeter. The heat produced by the combustion is absorbed by water circulating in the copper tubes. The rise in temperature, volume of gas burnt, volume of water circulated in the coils in time *t* and the mass of steam condensed help in finding the calorific value of the given fuel sample (for observation and calculation refer Junker's calorimeter).

Solved Examples

1. The following data were obtained in a Junker's calorimeter experiment

Volume of gas used	= 0.1 m^3 at STP
Wt of water heated	= 25 Kg
Temperature of inlet water	= 20°C
Temperature of outlet water	= 33°C
Weight of steam condensed	= 0.025 Kg

Calculate the higher and lower calorific value per m^3 at STP. Take the heat liberated in condensing water vapours and cooling the condensate as 580 Kcal/kg.

Solution

Here,

$V = 0.1\ m^3$; $W = 25$ kg; $T_2 = 33°C$; $T_1 = 20°C$; $m = 0.025$ kg.

$$\text{Therefore, } \text{HCV(H)} = \frac{W(T_2 - T_1)}{V} = \frac{25(33-20)}{0.1\,\text{m}^3} = 3250 \text{ Kcal/m}^3.$$

And LCV = HCV – $(m/V) \times 580$

$= 3250 \text{ Kcal/m}^3 - [(0.025 \text{ kg}/0.1 \text{ m}^3) \times 580 \text{ Kcal/kg}]$.

$= 3250 \text{ Kcal/m}^3 - 145 \text{ Kcal/m}^3 = 3105 \text{ Kcal/m}^3$.

Practice problems

1. During the determination of calorific value of a gaseous fuel by Boy's calorimeter, the following results were recorded

Volume of gaseous fuels burnt at NTP = 0.098 m^3

Weight of water used for cooling the combustion products = 50 kg

Weight of steam condensed = 0.051 kg

Temperature of inlet water = 26.1°C

Temperature of outlet water = 46.5°C

Latent heat of condensation of steam = 587 Kcal/kg

Determine the gross and net calorific values.

[Ans HCV/GCV = 10408.2 Kcal/m^3; NCV/LCV = 10102.7 Kcal/m^3]

Theoretical calculation of calorific value of a fuel

Dulong's assumed that the heat evolved comes from the combustion of carbon, hydrogen and sulphur present in the fuel, and the calorific value of the fuel is the sum of the calorific values of these constituents.

The calorific values of C, H and O is found to be 8080, 34500 and 2240 Kcal/kg, respectively.

Constituent	Higher calorific value
C	8080 Kcal/kg
H	34500 Kcal/kg
S	2240 Kcal/kg

If oxygen is also present, it combines with hydrogen to form H_2O. Thus, the hydrogen in combined form is not available for combustion and is called fixed hydrogen.

Amount of hydrogen available for combustion = Total mass of hydrogen–hydrogen combined with oxygen.

$$\underset{1}{H_2} + \underset{8}{\frac{1}{2}O_2} \rightarrow \underset{9}{H_2O}$$

i.e., 8 parts of oxygen combines with 1 part of hydrogen to form water or for every 8 parts of oxygen, 1 part of hydrogen gets fixed.

If the fuel contains *x* mass of oxygen then

$$\text{Fixed hydrogen} = \frac{1}{8} \times x = \frac{\text{Mass of oxygen in fuel}}{8}$$

$$\text{Amount of hydrogen available for combustion} = \left(H - \frac{O}{8}\right)$$

Dulong's formula for calculating calorific value is given as

$$\text{Gross calorific value (HCV)} = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]\text{Kcal/kg}$$

Here C, H, O and S are percentages of carbon, hydrogen, oxygen and sulphur in fuel.

$$\text{Net Calorific value (LCV)} = \left(HCV - \frac{9\,H}{100} \times 587\right)\text{Kcal/kg}$$

(HCV – 0.09 H × 587) Kcal/kg

(Latent heat of steam = 587 Kcal/Kg).

Solved Examples

Calculate the gross and net calorific values of coal having the following composition:
Carbon =85%; hydrogen = 8%; sulphur = 1%; nitrogen = 2%; ash = 4%
Latent heat of steam = 587 cal/g.

Solution

$$\text{Gross calorific value (HCV)} = \frac{1}{100}\left[8080\,\mathrm{C} + 34500\left(\mathrm{H} - \frac{\mathrm{O}}{8}\right) + 2240\,\mathrm{S}\right]\text{Kcal/kg}\,.$$

$$= \frac{1}{100}\left[8080 \times 85 + 34500\left(8 - \frac{0}{8}\right) + 2240 \times 1\right]\text{Kcal/kg}$$

$$= \frac{1}{100}\left[686{,}800 + 276{,}000 + 2240\right]\text{Kcal/Kg}$$

$$= \frac{1}{100}\left[965040\right]\ \text{Kcal/kg} = 9650.4\ \text{Kcal/kg}$$

LCV = (HCV – 0.09 H × 587) Kcal/kg

(9650.4 – 0.09 × 8 × 587) Kcal/kg = 9227.76 Kcal/kg.

Practice problems

1. A sample of coal has the following composition:
   Carbon =83%; hydrogen = 7.5%; sulphur = 1.5%; nitrogen = 0.6%; oxygen = 8.4%
   Find the gross calorific value using Dulong Formula.
   [Ans = 8965.25 Kcal/kg]
2. Calculate the gross and net calorific value of coal having the following composition
   Carbon =80%; hydrogen = 7%; sulphur = 3.5%; nitrogen = 2.1%; ash = 4.4 %
   Latent heat of steam = 587 Kcal/kg
   [Ans (i) 8828.02 Kcal/kg; (ii) 8458.21 Kcal/kg]

1.5 Solid Fuels

Solid fuel refers to various types of solid materials that are used as fuel to produce energy. The primary solid fuels commonly used are

Wood Wood is being used as fuel from times immemorial. Freshly cut wood contains 25 to 50% moisture which reduces to 15 % after drying the wood in air. The average composition of wood is: C = 55%; H = 6%; O = 43%; ash = 1%. Its calorific value is about 3500 – 4500 Kcal/kg. It burns with a long and non-smoky flame leaving behind small amount of ash.

Coal Coal is produced when the plant and animal debris are subjected to conditions of high temperature and pressure over millions of years. Hence, it is regarded as a fossil fuel. It chiefly comprises C, H, N and O besides non-combustible matter.

Classification and rank of coal

The different types of coal in increasing order of alteration are peat, lignite (brown coal immature), sub-bituminous, bituminous, and anthracite (mature). Coal starts off as **peat**. After being subjected to heat and pressure for a considerable amount of time, it is metamorphosed from peat to **lignite**. Lignite is referred to as brown coal because it is somewhat light in color and it remains soft. As time passes, lignite increases in maturity by becoming darker and harder and is then classified as **sub-bituminous** coal. As this process of burial and alteration continues, more chemical and physical changes occur and the coal is classified as **bituminous**. At this point the coal is dark and hard. **Anthracite** is the last stage of coal formation. Anthracite coal is very hard and shiny.

Table 1.2 Percentage composition of solid fuels

Fuel	Moisture of air dried sample at 40°C (%)	C (%)	H (%)	N (%)	O (%)	Calorific Value (Kcal/kg)
Wood	25	50.0	6.0	0.5	43.5	4000–4500
Peat	25	57.0	5.7	2.0	35.3	4125–5400
Lignite	20	67.0	5.0	1.5	26.5	6500–7100
Sub–bituminous coal	11	77.0	5.0	1.8	16.2	7000–7500
Bituminous coal	4	83.0	5.0	2.0	10.0	8000–8500
Semi–bituminous coal	1	90.0	4.5	1.5	4.0	8350–8500
Anthracite	1.5	93.3	3.0	0.7	3.0	8650–8700

Analysis of coal

The composition of coal varies widely. It is necessary to analyse and interpret the results for the purpose of price fixation, commercial classification and proper industrial utilization.

The quality of coal is ascertained by two types of analysis

- Proximate analysis
- Ultimate analysis

Proximate Analysis

It is an empirical but important analysis dealing with the determination of moisture contents, volatile matter, ash content and fixed carbon. It is called proximate analysis because the data vary with the procedure adopted. This analysis provides data for a general assessment of the quality and type of coal. It involves the following determinations

1. **Moisture Content**

A known weight of coal (air-dried) is taken in a crucible and heated in an electric hot air oven at about 105°C – 110°C for about one hour. After one hour, it is taken out from the oven and cooled in a dessicator and weighed. Loss in weight of the sample is found out and the percentage of moisture is calculated as follows

Let the weight of coal sample = W gm

Weight after heating for 1 hr = W_1 gm

Loss in weight i.e., the weight of moisture = $(W - W_1)$ gm

$$\% \text{ Moisture} = \frac{(W - W_1)}{W} \times 100$$

$$= \frac{\text{Loss in weight of the sample}}{\text{Weight of coal sample taken}} \times 100.$$

Significance

High moisture content is undesirable because it reduces the calorific value and increases the transportation cost.

- Presence of excessive moisture quenches fire in the furnace.
- A considerable amount of heat is wasted in evaporating the moisture during combustion.

2. **Volatile Matter**

The volatile matter present in the coal may be combustible gases such as H_2, CO, CH_4 and other hydrocarbons or non-combustible gases such as CO_2 and N_2. It *does not* include moisture of the coal.

It is determined by heating a known weight of moisture-free coal in a silica crucible covered with a vented lid at 950 ± 20°C for 7 minutes in a muffle furnace. The crucible is then taken out and cooled inside a dessicator and weighed again. Complete removal of volatile matter is judged by bubbling the gas through a water seal. Loss in weight gives the weight of the volatile matter and the percentage of volatile matter is calculated as follows

Let the weight of sample after removal of volatile matter = W_2 gm

Weight of volatile matter = $(W_1 - W_2)$ gm.

$$\% \text{ Volatile matter} = \frac{(W_1 - W_2)}{W} \times 100$$

$$= \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Weight of coal sample taken}} \times 100$$

Significance

- Coal containing high percentage of volatile matter burns with a long flame, high smoke and has low calorific value.
- A high percentage of volatile matter indicates that a large proportion of fuel is burnt as gas.
- Presence of non-combustible gases is undesirable since they do not add to the heat value.
- For efficient use of fuel, the outgoing combustible gas (volatile matter) has to be burnt by supplying secondary air. This requires a large combustion space.
- If the furnace volume is small or flame is short, a large proportion of volatile matter will escape unburnt.
- Coals with higher % of volatile matter do not cake well, whereas medium volatile coals containing 20–30% of volatile matter are capable of forming hard and strong coke on carbonization.
- Low volatile matter containing coals do not cake at all and are thus unsuitable for coke making.
- High volatile matter is desirable in coal gas manufacture because volatile matter in a coal denotes the proportion of coal that will be converted into gas and tar products by heat.
- However, for the manufacture of metallurgical coke, coal with low volatile matter content is preferred.

3. **Ash**

Ash is the non-combustible, useless matter that is left behind when all the combustible substances have burnt off from coal. Ash usually consists of silica, alumina, iron oxide and small quantities of lime, magnesia, etc.

Ash content is determined by heating the residue obtained after removal of moisture and volatile matter at 700 ± 50°C for half an hour without a lid in muffle furnace. The residue left is cooled in a dessicator and weighed. From the weight of residue, the percentage of ash is calculated as

Let the weight of ash formed = W_3 g.

$$\% \text{ ash} = \frac{W_3}{W} \times 100$$

$$= \frac{\text{Weight of ash formed}}{\text{Weight of coal sample taken}} \times 100$$

Significance

- High percentage of ash is undesirable as it reduces the calorific value of the fuel.
- Presence of ash increases the transporting, handling and storage cost.
- It also involves additional cost of ash disposal.

- Fused ash lumps (clinkers) block the interspaces of the grate, on which coal is being burnt. This causes obstruction in air supply. Hence, burning of coal becomes irregular. Hence, lower the ash content better the quality of the coal.

4. **Fixed Carbon**

   Fixed carbon is the material remaining after determination of moisture, volatile matter and ash content. It is determined indirectly by the formula

   Percentage of fixed carbon = 100 – % of (moisture + volatile matter + ash).

   Significance

   - Higher the percentage of fixed carbon, greater is the calorific value.
   - The percentage of fixed carbon helps in designing the furnace because it is the fixed carbon that burns in the solid state.

Solved Examples

A sample of coal was analysed as follows. Exactly 2.500 g was weighed into a silica crucible. After heating for an hour at 110°C, the residue weighed 2.415 g. The crucible was then covered with a vented lid and strongly heated for exactly 7 min at 950 ± 20°C. The residue weighed 1.528 g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weigh 0.245 g. Calculate the % of moisture, volatile matter, ash and fixed carbon in the coal sample.

Solution

(i) *Percentage of moisture*

Weight of coal sample taken = 2.500 g

Weight after heating at 110°C = 2.415 g

Loss of weight = weight of moisture = 2.500 – 2.415 = 0.085g

$$\% \text{ moisture } = \frac{\text{weight of moisture}}{\text{weight of coal taken}} \times 100$$

$$= \frac{0.085}{2.500} \times 100 = 3.4\%$$

% moisture = 3.4%

(ii) *Percentage of volatile matter*

Weight of residue after heating at 950°C = 1.528 g

Loss of weight = weight of volatile matter = 2.415 – 1.528 = 0.887g.

$$\% \text{ volatile matter} = \frac{\text{weight of volatile matter}}{\text{weight of coal sample taken}} \times 100$$

$$= \frac{0.887}{2.500} \times 100 = 35.48$$

% volatile matter = 35.48%

(iii) *Percentage of ash*

$$\frac{\text{weight of residue left}}{\text{weight of coal sample taken}} \times 100$$

$$\frac{0.245}{2.5} \times 100 = 9.8\%$$

% ash = 9.8%

(iv) *Percentage of fixed carbon* = 100 – % of (moisture + volatile matter + ash)

= 100 – (3.4 + 35.48 + 9.8)

= 100 – 48.68 = 51.32%

% fixed carbon = 51.32%

Practice problems

1. A sample of coal was analysed as follows

   Exactly 1.500 g was weighed into a silica crucible. After heating for an hour at 110°C, the residue weighed 1.415 g. The crucible was then covered with a vented lid and strongly heated for exactly 7 min at 950 ± 20°C. The residue weighed 0.528 g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weigh 0.254 g. Calculate

   (i) The percentage results of the above analysis.

   (ii) To which type of analysis does the above description belong ? Why the above analysis is named so?

   [Ans Moisture = 5.67%; volatile matter = 59.13%; ash = 16.93 %; fixed carbon = 18.27%]

2. A sample of coal was analysed as follows

   Exactly 2.000 g was weighed into a silica crucible. After heating for an hour at 110°C, the residue weighed 1.975 g. The crucible was then covered with a vented lid and strongly heated for exactly 7 min at 950 ± 20°C. The residue weighed 1.328 g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weigh 0.204 g. Calculate

   The percentage results of the above analysis.

   [Ans Moisture = 1.25%; volatile matter = 32.35%; Ash = 10.20 %; fixed carbon = 56.20%]

Ultimate analysis

It is also called elemental analysis and is used for the determination of carbon, hydrogen, nitrogen, sulphur and oxygen. This analysis requires high degree of skill and the equipments are expensive. However, it gives exact results that are useful in calculating the calorific value of coal using *Dulong's Formula*.

1. ***Carbon and hydrogen*** Accurately weighed coal sample is burnt in a combustion tube in a current of O_2 (free from CO_2 and moisture). The carbon and hydrogen present in the fuel is converted to CO_2 and H_2O respectively. These are then absorbed by previously weighed tubes containing KOH and anhydrous $CaCl_2$. The increase in weights of these tubes gives the amount of CO_2 and H_2O formed. % of C and H is then calculated as follows

$$C + O_2 \rightarrow CO_2$$

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

$$H_2 + ½\, O_2 \rightarrow H_2O \qquad CaCl_2 + 7H_2O \rightarrow CaCl_2 . 7H_2O.$$

Let the weight of coal sample taken = x gm.

Increase in weight of KOH tube = y gm.

Increase in weight of $CaCl_2$ tube = z gm.

Now,

44 gm of CO_2 contains 12 gm of C.

y gm of CO_2 contains $\frac{12}{44} \times y$ gm of C.

$$\% \text{ Carbon} = \frac{12}{44} \times \frac{y}{x} \times 100$$

$$\text{or, percentage of carbon} = \frac{12}{44} \times \frac{\text{Increase in weight of KOH tube}}{\text{weight of coal sample taken}} \times 100$$

Similarly,

18 gm of H_2O contains 2 gm of H

z gm of H_2O contains $\frac{2\times z}{18}$ gm of H

$$\% \text{ of Hydrogen} = \frac{2}{18}\times\frac{z}{x}\times 100$$

$$\text{Percentage of hydrogen} = \frac{2}{18}\times\frac{\text{Increase in weight of } CaCl_2 \text{ tube}}{\text{Weight of coal sample taken}}\times 100$$

Significance

- Calorific value of a fuel is directly related to the carbon contents; hence, greater the percentage of carbon, greater is the calorific value of the fuel.
- % of carbon increases from lignite to anthracite; thus, the % of carbon forms the basis of classification of coal.
- High percentage of hydrogen also increases the calorific value of coal. However, hydrogen is mostly associated with volatile matter and affects the use to which coal is put.
- In carbonization and gasification industries, hydrogen of coal is responsible for the production of many useful materials such as gaseous hydrogen, methane etc.

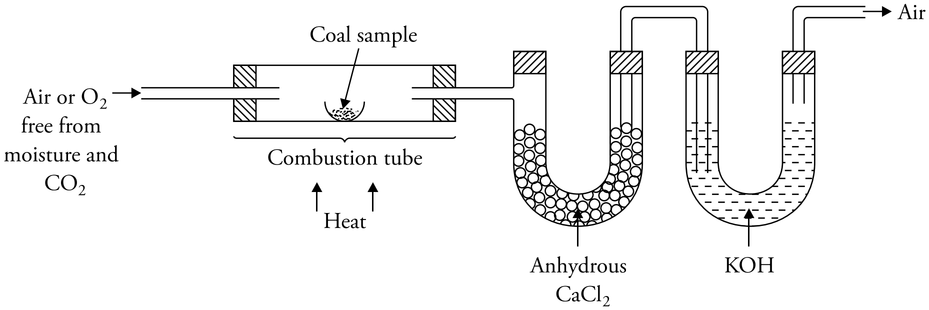

Figure 1.5 *Determination of carbon and hydrogen*

2. ***Nitrogen*** Nitrogen present in coal sample is estimated by Kjehldahl's Method
    - Accurately weighed coal sample is heated with concentrated H_2SO_4 in the presence of K_2SO_4 in a long–necked flask known as Kjehldahl's flask. Nitrogen present in the coal gets converted to $(NH_4)_2SO_4$ quantitatively.

$$\underset{\text{(from Coal)}}{\text{Nitrogen}} + H_2SO_4 \xrightarrow{\text{heat}} (NH_4)_2SO_4$$

- When a clear solution is obtained (i.e., whole nitrogen is converted into ammonium sulphate), the contents are transferred into a round bottom flask and the solution is heated with excess of NaOH to liberate NH_3.
- The NH_3 thus liberated is absorbed in a known volume of a standard H_2SO_4 solution (N/10).
- The volume of unused H_2SO_4 is determined by titrating against standard NaOH solution (N/10). Difference gives the volume of acid used. From the volume of acid used by NH_3, the percentage of nitrogen can be calculated.

$$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + Na_2SO_4 + 2H_2O$$

$$NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

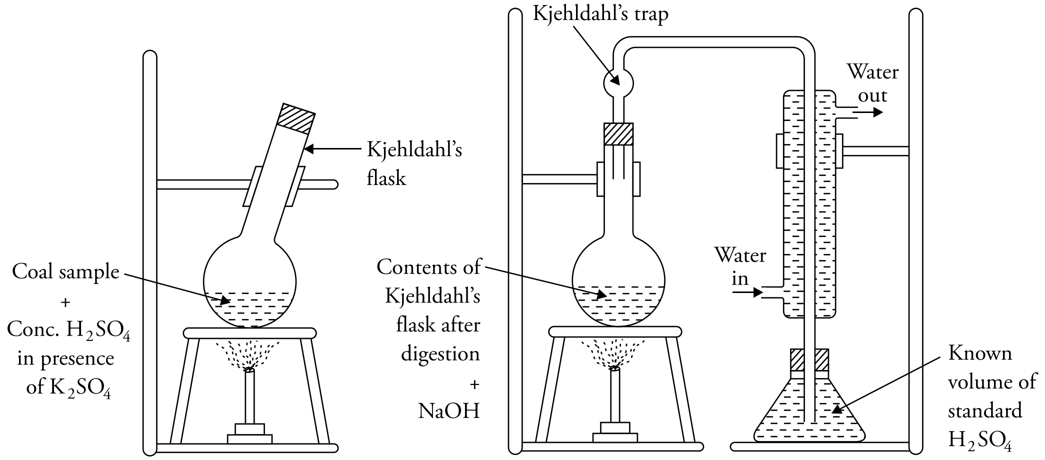

Figure 1.6 *Estimation of nitrogen*

Let the weight of coal taken = W gm

Volume of acid used = V_1 ml

Normality of acid = N_1

As we know,

Equivalents of H_2SO_4 used = Equivalent of NH_3 formed

∵ Equivalents of H_2SO_4 used = N_1V_1

Hence, equivalents of NH_3 formed = N_1V_1

Now,

Normal (1N solution of NH_3 means 1 gm equivalent NH_3 in 1 litre

$\therefore$ 1000 ml contains 17 gm $NH_3 \equiv$ 14 gm nitrogen.

N_1V_1 of NH_3 will contain $= \frac{14}{1000} \times N_1V_1$ nitrogen.

$$\% \text{ Nitrogen} = \frac{14}{1000} \times \frac{N_1V_1}{W} \times 100 .$$

$$\% \text{ Nitrogen} = \frac{1.4 \times \text{Normality of } H_2SO_4 \times \text{Volume of } H_2SO_4 \text{ used}}{\text{Weight of coal sample taken}}$$

Significance

- Since nitrogen is an inert and incombustible gas with no calorific value, its presence in fuel is undesirable.

3. **Sulphur**

A known amount of coal is burnt completely in a bomb calorimeter in a current of oxygen. Sulphur in the coal is oxidized to sulphates. The ash from the bomb calorimeter is extracted with dilute hydrochloric acid. The acid extract is then treated with $BaCl_2$ solution to precipitate sulphate as $BaSO_4$. The precipitate of $BaSO_4$ is filtered, washed, dried and heated to a constant weight. From the weight of $BaSO_4$ formed, S is estimated as follows

$$\underset{32}{S} \xrightarrow{O_2} SO_4^{2-} \xrightarrow{BaCl_2} \underset{233}{BaSO_4}$$

Let the weight of coal sample = W gm

Weight of $BaSO_4 = x$ gm

$\because$ 233 gm of $BaSO_4$ = 32 g of S

$\therefore$ x gm of $BaSO_4 = \frac{32}{233} \times x$

$$\% \text{ S} = \frac{32}{233} \times \frac{x}{W} \times 100$$

$$\text{or } \% \text{ S} = \frac{32}{233} \times \frac{\text{Weight of } BaSO_4}{\text{Weight of coal taken}} \times 100 .$$

Significance

- Although sulphur increases the calorific value of fuel, yet its presence is undesirable because it gets oxidised to SO_2 and SO_3, which causes environmental pollution.
- Sulphur-containing coal is not suitable for preparing metallurgical coke. Presence of sulphur in coke used in the iron industry affects the quality and properties of steel.

4. **Ash** It is determined in the same way as in proximate analysis.
5. **Oxygen** It is determined indirectly by deducting the % of C, H, N, S and ash from 100% of oxygen = 100 – % of (C + H + N + S + ash).

Significance

- Oxygen is present in coal in combined form. It is present in association with hydrogen; hence, it reduces the hydrogen available for combustion.
- Moreover, high oxygen-containing coals have high inherent moisture and hence low calorific values.
- Calorific value decreases about 1.7% for every 1% increase in oxygen.

Thus, a good-quality coal should have low % of oxygen.

Solved examples

1. 0.25 g of a sample of coal was analyzed by combustion method. The increase in weights of $CaCl_2$ tube and the potash bulbs at the end of the operation was found to be 0.15 g and 0.55 g, respectively. Calculate the percentage of carbon and hydrogen in the coal.

Solution

Weight of CO_2 (increase in weight of KOH bulb) = 0.55 g.

Weight of H_2O (increase in weight of $CaCl_2$ tubes) = 0.15 g.

$$\underset{12}{C} + O_2 \rightarrow \underset{44}{CO_2}$$

44 g CO_2 contains carbon = 12 g

$$0.55 \text{ g } CO_2 \text{ contains carbon} = \frac{12}{24} \times 0.55 \text{ g}$$

$$\text{Percentage of carbon} = \frac{12 \times \text{weight of carbondioxide}}{44 \times \text{weight of coal sample taken}} \times 100$$

$$= \frac{12}{44} \times \frac{0.55}{0.25} \times 100 = 60\%$$

Percentage of carbon = 60%.

To calculate % of hydrogen,

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

2 g 18 g

18 g H_2O contains hydrogen = 2 g

0.15 g H_2O contains hydrogen = $\frac{2}{18} \times 0.15$

Percentage of hydrogen $= \frac{2}{18} \times \frac{0.15}{0.25} \times 100 = 6.67\%$

Percentage of hydrogen = 6.67 %

2. 1.0 g of a coal sample was used in a bomb calorimeter for the determination of calorific value. Calorific value of coal was found to be 8800 cal/g. The ash formed in the bomb calorimeter was extracted with acid and the acid extract was heated with $BaCl_2$ solution and a precipitate of $BaSO_4$ was obtained. The precipitate was filtered, dried and weighed. The weight of precipitate was found to be 0.08 g. Calculate the percentage of sulphur in the coal sample.

Solution

$$\text{Percentage of sulphur} = \frac{\text{weight of } BaSO_4 \text{ ppt obtained} \times 32 \times 100}{233 \times \text{weight of coal sample taken}}$$

$$= \frac{0.08 \times 32 \times 100}{233 \times 1} = 1.0987\%$$

Percentage of sulphur = 1.0987 %

3. 0.3 g of coal sample on Kjehldahl's analysis gave ammonia to just neutralize 30 ml of 0.1 N H_2SO_4. Calculate the percentage of nitrogen in the coal sample.

Solution

Weight of coal sample = 0.3 g

Volume of H_2SO_4 used = 30 ml

Normality of H_2SO_4 = 0.1 N

$$\text{Percentage of Nitrogen} = \frac{\text{volume of } H_2SO_4 \text{ used} \times \text{normality} \times 1.4}{\text{weight of coal sample taken}}$$

$$= \frac{30 \times 0.1 \times 1.4}{0.3} = 14\%$$

Percentage of nitrogen = 14%

4. 1.56 g of a coal sample was Kjehldahlized and NH_3 gas thus evolved was absorbed in 50 ml of 0.1 N H_2SO_4. After absorption, the excess (residual) acid required 6.25 ml of 0.1 N NaOH for exact neutralization. Calculate the percentage of nitrogen in the coal sample.

Solution

Weight of coal sample taken = 1.56 g

Since, 6.25 ml of 0.1N NaOH is used for neutralization, hence excess acid

= 6.25 ml of 0.1 N H_2SO_4.

Therefore, Volume of H_2SO_4 used to neutralize NH_3 evolved

= 50 ml of 0.1N – 6.25 ml of 0.1 N H_2SO_4

= (50–6.25)× 0.1 N H_2SO_4

= 43.75 ml of 0.1 N H_2SO_4

$$\text{Percentage of nitrogen} = \frac{\text{Volume of } H_2SO_4 \text{ used} \times \text{normality of } H_2SO_4 \times 1.4}{1.56} = 3.926\%$$

$$\frac{43.75 \times 0.1 \times 1.4}{1.56} = 3.926$$

Percentage of nitrogen = 3.926%

Practice problems

1. 0.26 g of a sample of coal analyzed by combustion gave 0.039 g of water and 0.245 g of carbon dioxide. Calculate the percentage of carbon and hydrogen in the coal.

   (Ans % of carbon = 25.69%: % hydrogen = 1.66%)

2. 0.1 g of a sample of coal was used in a bomb calorimeter for the determination of calorific value. The ash formed was extracted with acid and the acid extract was heated with $BaCl_2$ solution and a precipitate of $BaSO_4$ was obtained. The precipitate was filtered, dried and weighed. The weight of precipitate was found to be 0.01 g. Calculate the percentage of sulphur in the coal sample. (Ans % sulphur = 1.3734%)

3. 3.12 g of the coal sample was Kjehldahlized and NH_3 gas was absorbed in 50 ml of. 0.1N H_2SO_4. After absorption, the excess (residual) acid required 12.5 ml of 0.1 N NaOH for exact neutralization. Determine the percentage of nitrogen in the coal sample.

   (Ans % nitrogen = 1.683%)

4. 3.0 g of the coal sample was Kjehldahlized and NH_3 gas was absorbed in 45 ml of 0.1N H_2SO_4. After absorption, the excess (residual) acid required 8.5 ml of 0.1 N NaOH for exact neutralization. Determine the percentage of nitrogen in the coal sample.

   (Ans % nitrogen = 1.7033%)

Carbonization of coal

When coal is heated to a high temperature in the absence of air, it loses volatile matter and gets converted into a white, dense, lustrous, strong, porous and coherent mass, which is richer in carbon content than the original fuel. This is known as *coke* and the process of converting coal into coke in the absence of air is known as *carbonization of coal.*

Process of carbonization

The process of carbonization can be depicted with the help of the flow chart given below

Bituminous Coals

↓

Moisture and occluded gases are driven off

↓

H_2O, H_2S, some low molecular weight alkenes and alkanes are evolved

↓ 350°C

Decomposition of coal accompanied by the evolution of gases and elimination of tarry vapours takes place

↓ 400°C

Caking coal becomes soft and plastic

↓ 700°C

Hydrogen is evolved

↓ 800°C

Gases evolved form the plastic mass and expand to give foam-like appearance

↓ > 800°C

Coke is formed by solidification of this foam-like mass

Caking and coking coals

It is important to note that all types of coals cannot be converted into coke. Some coals soften and form a plastic mass that swells and resolidifies into a porous solid. Such coals are called caking coals. When this porous solid is quenched, it results in the formation of a strong residue called coke. If the coke formed is hard, porous and strong, then the coal from which it is formed is called coking coal. Coking coal is also called metallurgical coke. This is a unique property of bituminous coal; hence, only bituminous coals can be converted into coke. Anthracite, sub-bituminous, lignite coals are non-coking coals. All coking coals are caking coals; however, only some caking coals fall under the category of coking coals.

Generally, coals with a high percentage of volatile matter, lower ash and higher fixed carbon content are not fit for 'coking'. The coals having 20–30% volatile matter are good coking coals.

Pulverised coal

Usually the rate of combustion of coal is very slow. This can be increased either by

(i) Increasing the rate of supply of air; however, it results in the wastage of heat, as heat is carried away along with the current of air.

(ii) Increasing the surface area of coal by powdering it. The powdered coal comes in contact with larger amount of oxygen and hence it burns readily.

This powdered coal is called pulverized coal. Generally, pulverization is carried out for coals containing large amount of volatile matter. The volatile matter gets liberated out more quickly from the powder rather than from larger lumps of coal.

Advantages of pulverized coal

1. Its handling and transportation is easier. The transportation can be carried out by forcing a stream of air or by screw conveyor.
2. Combustion of pulverized coal is complete and uniform, as it gets intimately mixed with air.
3. The excess air needed for combustion is less than that needed for solid fuels.
4. The volatile matter is easily removed.
5. Rate of combustion can be controlled easily as in case of liquid and gaseous fuels.
6. There is no clinker formation in pulverized coal.

Disadvantages of pulverized coal

1. Additional cost is involved for pulverizing and sieving the fuel.
2. The ash formed by burning of pulverized coal is in finely divided state. It is called 'Fly Ash' and it creates serious environmental problems.
3. Pulverized coal produces long flame and hence large combustion space is required.

Types of carbonization

The properties of the coke produced depend on the type of coal used, temperature and the rate of carbonization. Depending upon the temperature, carbonization is of two types

1. Low-temperature carbonization
2. High-temperature carbonization

(i) ***Low temperature carbonization*** When destructive distillation of coal is carried out at 500-700°C, it is called low temperature carbonization. It is used mainly for the manufacture of domestic fuel.

The yield of coke is about 75–80 %. The coke thus produced contains 5–15 % volatile matter and is not strong enough to be used as metallurgical fuel. It is highly reactive, easily ignited and is a valuable, smokeless domestic fuel. In low-temperature carbonization, the amount of liquid products is relatively larger. The gas obtained as a byproduct during low-temperature carbonization has high calorific value of about 6500–9500 Kcal/m^3 and the yield is about 130–150 m^3/tonn of the coal carbonized. It is a valuable gaseous fuel.

The tar obtained as a byproduct contains more of paraffinic hydrocarbons and small amount of aromatic hydrocarbons along with phenols and various other nitrogenated compounds.

There are two major commercial LTC plants in India. One is in Neyveli /Tamil Nadu and other is in Andhra Pradesh

(ii) ***High temperature carbonization*** It is carried out at 900°C – 1200°C and is used for the production of pure, hard, strong and porous metallurgical coke containing 1–3% volatile matter. The yield of coke is 65–75%.

The byproduct gas and tar have greater amount of aromatic hydrocarbons. The yield of byproduct gas is 370–480 m^3/tonn of coal carbonized but its calorific value is lower (5000–6000 Kcal/m^3) than that produced in LTC. The formation of lower amount of paraffins and higher amount of gas, indicates that cracking of paraffinic compounds present in coal takes place at high temperature, resulting in the formation of gases and greater aromatization.

Table 1.3 Comparison between low and high-temperature carbonization

S.No	Characteristic	Low-Temperature Carbonization	High-Temperature Carbonization
1	Carbonization Temperature	About 500–700°C	900–1200°C
2	Yield	75–80 %	65–75 %
3	Volatile matter content in coke	5–15 %	1–3 %
4	Mechanical strength of coke	Poor	Good
5	Hardness	Soft coke	Hard coke
6	Use of Coke	For domestic purposes	For metallurgical purposes
7	Smoke produced on burning	Smokeless	Smoky
8	Yield of byproduct gas	Lower (130–150 m^3/ tonn of coal carbonized)	Higher (about 370–480 m^3/ tonn of coal carbonized)
9	Calorific value of byproduct gas	6500–9500 Kcal/m^3	5000–6000 Kcal/m^3
10	Percentage of straight chain hydrocarbon in byproducts (tar and gas)	Higher	Lower
11	Percentage of aromatics in the byproducts	Lower	Higher

Metallurgical coke

Coke is used as a heat source and reducing agent in metallurgy. Its properties depend on porosity, reactivity and the amount of volatile matter retained by coke during carbonization. A good metallurgical coke should possess the following properties

(i) ***Purity*** The moisture, ash, sulphur and phosphorus contents should be very low. Moisture reduces calorific value whereas excess of ash hinders the heating and also helps in slag formation. Presence of sulphur and phosphorus gives undesirable products like SO_2, P_2O_3 and P_2O_5 on burning which adversely affect the quality of the metal being produced. Presence of sulphur makes the coke brittle.

(ii) ***Porosity*** Coal should be porous, so that oxygen can come in contact with carbon which ensures efficient and complete combustion of the fuel in the furnace.

(iii) ***Strength*** Coke should be compact, hard, strong enough to withstand high pressure in the furnace as well as to withstand the abrasive action of the ores, flux, etc.

(iv) ***Size*** Metallurgical coke should be of medium size – neither too big nor too small. If the size is big, uniform heating is not possible whereas small size of coke results in choking.

(v) ***Combustibility*** Coke should burn easily but at the same time it should not be very reactive.

(vi) ***Calorific Value*** The calorific value of coke should be high.

(vii) ***Cost*** It should be cheap and easily available.

(viii) ***Calorific intensity*** The calorific intensity of coke should be high enough to melt the metal.

Manufacture of metallurgical coke

Metallurgical coke can be manufactured by two methods:
(i) Beehive Oven method
(ii) Otto Hofmann's oven or By-product oven or Chamber oven method.

Beehive oven method

It is the earliest and cheapest method for the manufacture of metallurgical coke.

Construction It is a dome-shaped structure made up of bricks. It is about 4 m wide and 2.5 m high. It has two openings, one at the roof for charging the coal from the top and the other at the side for the entry of air and also for the removal of coke.

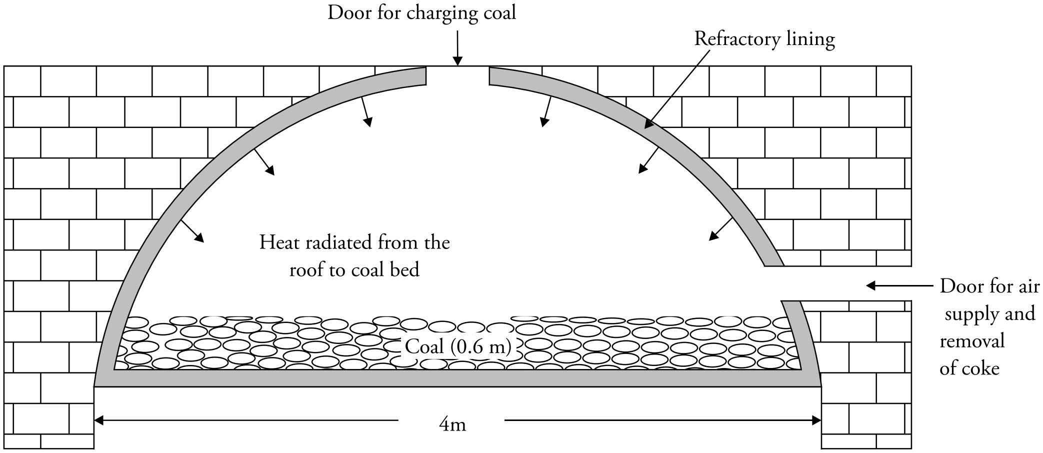

Figure 1.7 *Beehive coke oven*

Process The coal is introduced from the top hole of the dome and is spread evenly on the floor to give a layer of about 0.6–0.75 m thickness. The coal is ignited and just sufficient air is admitted through the side opening to maintain the desired temperature. Carbonization starts and the volatile matter burns inside the partially closed side door. Carbonization proceeds from top to bottom and is completed in about 3 days. The oven is allowed to cool and the hard metallurgical coke formed is quenched with water and taken out through the discharge side door. The walls and roofs of the emptied oven are hot enough to start the carbonization of the next batch. The yield of coke is about 60–80% and averages 5–6 tonn coke per oven.

The process can be made more economical by operating a series of Beehive's ovens in such a way that hot gases escaping from one oven are utilized to ignite the charge in the adjacent oven.

Limitations of the process

- Coke yield low.
- Most volatile matter having many valuable byproducts escapes into the atmosphere as waste.
- The exhaust gases cause pollution.
- Process is not flexible.

Otto Hofmann's oven or Byproduct oven or Chamber oven

Construction It consists of a number of narrow rectangular chambers made of silica bricks. Each chamber is 10–12 m long, 3–4 m high and 0.4–0.45 m wide. The chambers are tightly closed so that no air is admitted. At the top of each chamber, there are three holes for charging the coal. It is also provided with a gas take off (which carries out volatile matter) and discharging doors at the base for the removal of coke. These carbonization chambers are erected side by side with interspaces for combustion of fuel gas. Thus, the ovens get heated from both sides. The ovens (chambers) form a sort of battery of 10–100 ovens. One single oven is capable of holding 16–24 tonnes of coal.

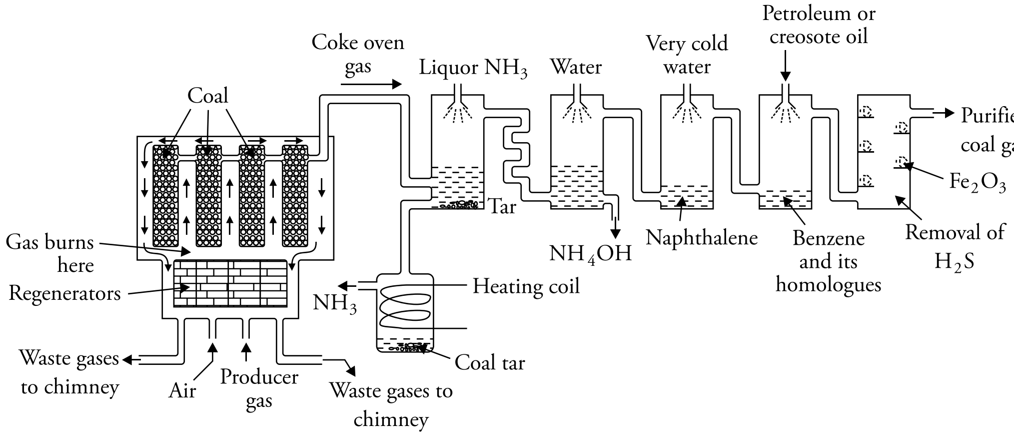

Figure 1.8 *Otto Hofmann's coke oven method*

Working

Finely crushed coal is introduced through the charging holes at the top of the chambers which are then closed tightly at both ends to cut off the supply of air. The ovens are heated to 1200°C by burning gaseous fuels (such as producer gas). ***Regenerative principle* of heat economy is employed to achieve as economical heating as possible.

The process of carbonization starts in coal adjacent to the walls and moves towards the centre. As the coal is converted into coke, there is decrease in volume due to removal of volatile matter.

Carbonization of a charge of coal takes about 11–18 h. After the process is complete, red hot coke is pushed out by means of a ram, which is electrically driven. The coke falls into a quenching car.

Quenching of red hot coke is carried out either by spraying water (wet quenching) or by passing inert gas such as N_2 from boilers (dry quenching). In wet quenching, sensible heat of coke is wasted, whereas in dry quenching the inert gases after quenching the coke become heated up and are circulated to the boilers where they generate steam. The coke produced by dry quenching is more strong, dense, graphitized and non-reactive. It is cheaper, dry and contains less dust than the wet quenched coke.

Recovery of by products

The gas coming out of the oven is known as 'coke oven gas' and is mainly composed of ammonia, H_2S, naphthalene, benzene, tar, moisture, etc. These are recovered as follows

(i) ***Recovery of Tar*** The gases from the coke oven are passed through a tower in which liquor ammonia is sprayed. Tar and dust get collected in a tank below. The tank is provided with heating coils to recover NH_3. Ammonia is again sent to the top of the trickling tower and is used again.

(ii) ***Recovery of ammonia*** The gases now enter another tower where water is sprayed. Ammonia goes into the solution as NH_4OH.

(iii) ***Recovery of naphthalene*** The gases then pass to a cooling tower where water at low temperature is sprayed. Naphthalene gets condensed which is then collected.

(iv) ***Recovery of benzene*** The gases then pass through a scrubber, where petroleum is sprinkled, resulting in the condensation of benzene and its homologues.

(v) ***Recovery of H_2S*** The gases then enter a purifying chamber packed with moist Fe_2O_3. Here H_2S is retained.

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* *Regenerative principle is employed to achieve as economical heating as possible. In this the flue gases(waste gases produced after combustion) are passed through regenerators and then let off into the atmosphere through chimneys. Regenerators are built underneath the ovens. The flue gases pass their heat to the checker brick work of regenerators until the temperature rises to about 1000°C. The flow of heating flue gases is then reversed and the inlet gas(fuel gas and air) used for combustion is passed through the heated checker brickwork of regenerators. Thus the inlet gases are preheated. After sometime again the flow of gases is reversed to heat the checker work. Hence the regenerator works on the principle of alternate heating and cooling cycles.*

$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O$

After sometime, when all Fe_2O_3 is changed to Fe_2S_3, the purifier is exposed to atmospheric air, where Fe_2O_3 is regenerated.

$Fe_2S_3 + 4O_2 \rightarrow 2\ FeO + 3SO_2 \uparrow$

$4FeO + O_2 \rightarrow 2\ Fe_2O_3$

(vi) ***Recovery of gas*** The gas after passing through various condensers and scrubbers to remove the byproducts mentioned above is finally collected in a gas holder. It is the coal gas whose calorific value is about 5000 Kcal/m^3.

1.6 Liquid Fuels

Liquid fuels are used extensively in industrial and domestic fields. Use of liquid fuels in internal combustion engines makes them very important fuels. The single largest source of liquid fuels is petroleum or crude oil (the term petroleum means rock oil. Latin-Petra means rock; oleum means oil) is a dark, greenish-brown viscous oil found deep inside the earth's crust. It is a mixture of hydrocarbons such as straight chain paraffins, cycloparaffins or naphthalene, olefins and aromatics along with small amount of organic compounds containing oxygen, nitrogen and sulphur.

Average composition of crude petroleum is

Element	Carbon	Hydrogen	Sulphur	Nitrogen	Oxygen
Percentage	75.5–87.1%	11.5–14.8%	0.1–3.5%	0.4–0.9%	0.1–0.9%

Classification of petroleum

Petroleum is classified into three categories according to its composition

1. ***Paraffinic base petroleum*** It is mainly composed of straight chain saturated hydrocarbons from CH_4 to $C_{35}H_{72}$ along with small amounts of naphthenes and aromatic hydrocarbons.
2. ***Naphthenic or asphaltic base petroleum*** It contains mainly cycloparaffins or naphthenes as main constituent along with smaller amount of paraffins and aromatic hydrocarbons.
3. ***Mixed base petroleum*** It contains both paraffins and asphaltic hydrocarbons.

Table 1.4 Classification of Crude Petroleum

Type of petroleum	**Constitution**	**Residue obtained after distillation**	**Remarks**
Paraffinic base petroleum	Straight chain saturated hydrocarbons from CH_4 to $C_{35}H_{72}$ along with small amounts of naphthenic and aromatic hydrocarbons.	Solid paraffin wax	Furnish low octane number straight run gasoline

Naphthenic or asphaltic base petroleum	Cycloparaffins or naphthenes as main constituent along with smaller amount of paraffins and aromatic hydrocarbons.	Asphalt or bitumen	Furnish high octane number straight run gasoline
Mixed base petroleum	Both paraffins and asphaltic hydrocarbons	Paraffin wax and asphalt	Furnish medium grade straight run gasoline

Mining of petroleum

Petroleum is found deep below the earth's crust. The oil is found to be floating over salt water or brine and has a layer of gas on top of it. Mining of oil is carried out by drilling holes in the earth's crust and sinking pipes up to the oil-bearing porous rocks. Oil rushes through these holes because of the pressure of natural gas. As the pressure of natural gas subsides, the oil is pumped out with the help of air lift pumps.

The air lift pump is a device containing two co-axial pipes lowered into the oil bed. The compressed air is forced through the outer pipe causing the oil to flow out through the inner pipe. This oil is then led to the refinery and processed.

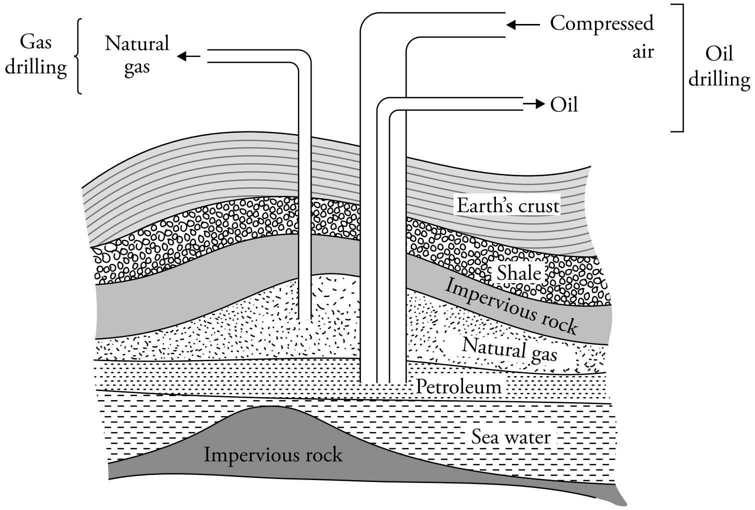


Figure 1.9 *Mining of petroleum*

Refining of petroleum

Crude oil coming out from the oil well is a mixture of solid, liquid and gaseous hydrocarbons containing sand and water in suspension. After removal of dirt, water, sulphur and other impurities, this oil is subjected to fractional distillation. This process of removing unwanted impurities and dividing petroleum into useful fractions with different boiling ranges is called *Refining of Petroleum.* The process of refining involves the following steps

1. ***Separation of water (Demulsification)*** The crude oil from the well is an extremely stable emulsion of oil and salt water. The demulsification is achieved by *Cotrell's process.* The crude oil is allowed to flow between two highly charged electrodes where colloidal water droplets coalesce to form large drops which separate out from the oil.
2. ***Removal of harmful impurities*** NaCl and $MgCl_2$ corrode the refining equipments. These are removed by modern techniques like electrical desalting and dehydration.

   Harmful sulphur compounds are removed by treating the crude oil with copper oxide. Sulphur reacts with copper oxide forming copper sulphide, which is removed by filtration.
3. ***Fractional Distillation*** The crude oil is heated to 400°C in an iron retort whereby all the volatile constituents, except asphalt or coke are evaporated. The vapours are then passed into a fractionating column, which is a tall cylindrical tower. The tower is hot towards the lower end and comparatively cooler at the upper end. It consists of a number of horizontal stainless steel trays at short distances. These trays are provided with individual chimneys which are covered with a loose cap. As the vapours go up, fractional condensation occurs at different heights of the column. Higher boiling fractions condense first, while lower boiling fractions condense later as shown in Fig 1.10.

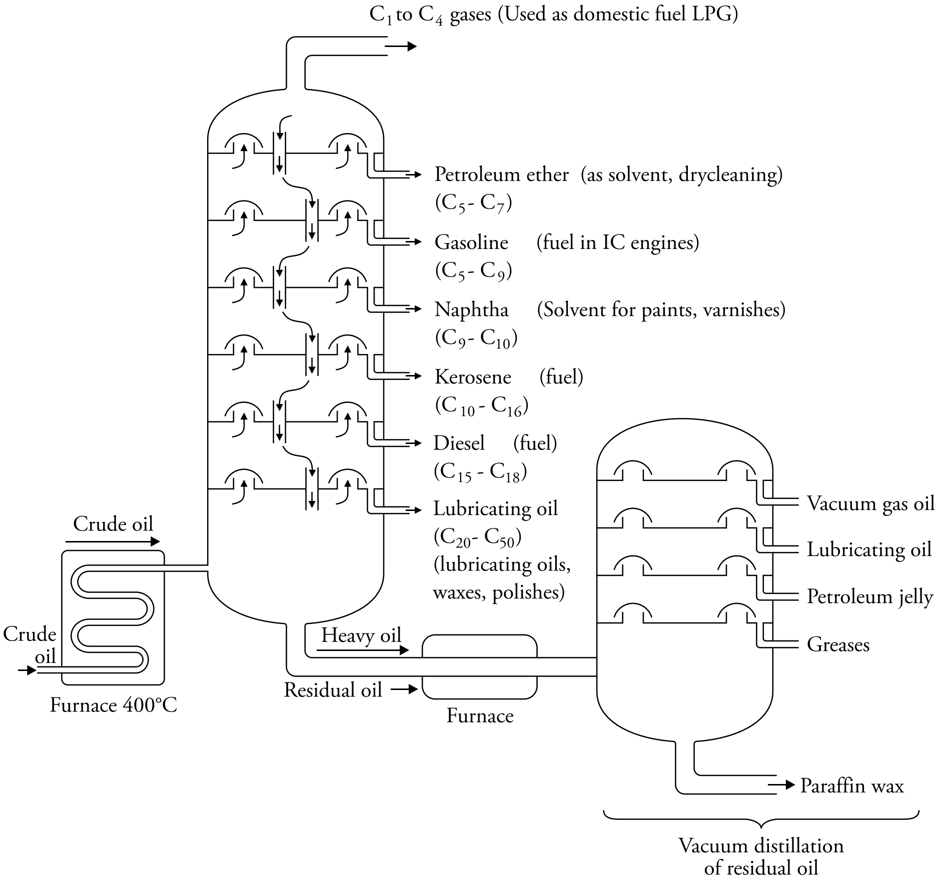


Figure 1.10 *Fractional distillation of crude oil*

The residue from the bottom of fractionating tower is vacuum-distilled to recover various fractions.

The names, approximate composition, range and uses of various fractions are given below in the table 1.5.

Table 1.5 Major fractions obtained by the distillation of crude oil

S.No	Fraction's name	Boiling Temperature	Approximate composition in terms of hydrocarbons containing C atoms	Uses
1	Uncondensed gases	Below 30°C	C_1–C_4	Used as domestic fuel (LPG)
2	Petroleum ether	30–70°C	C_5–C_7	Solvent for fats, essential oils, used in dry cleaning.
3	Gasoline or petrol or motor spirit	70–120°C	C_5–C_9	As a motor fuel for IC engines, as a solvent and in dry cleaning.
4	Naphtha or solvent spirit	120–180°C	C_9–C_{10}	As a solvent for paints and varnishes and in dry cleaning.
5	Kerosene oil	180–250°C	C_{10}–C_{16}	Fuel for stoves, jet engine fuel and for preparing oil gas used in laboratories.
6	Diesel oil	250–320°C	C_{15}–C_{18}	Diesel engine fuel
7	Heavy oil Heavy oil on vacuum distillation gives i. Lubricating oil ii. Petroleum jelly (vaseline) iii. Greases iv. Paraffin wax	320–400°C – – – –	C_{17}–C_{30} C_{17}–C_{20} – C_{20}–C_{28}	Fuel for ships, in metallurgical furnaces and in conversion to gasoline by cracking. As lubricants Used in cosmetics and medicines As lubricant In candles, boot polishes, wax paper, etc
8	Residue: It may be either i. Asphalt(if the crude oil is asphaltic) ii. Petroleum Coke	> 400°C	C_{30} and above	Used for water proofing of roofs and for road making. As a fuel in moulding electrode rods for cells.

The gasoline obtained by this fractionation is called *straight run gasoline*

Cracking

The crude oil obtained on fractionation yields approximately 20–30% gasoline, 30–35% middle oils and 20–25% heavy oils. Among all these fractions, gasoline (also called straight run petrol) is in maximum demand because of its use as fuel in the automobile industry. Hence, there is a need to convert the middle oil and heavy oil fractions of gasoline into a more useful fraction gasoline. This is achieved by *cracking*.

Cracking is defined as the process of converting high molecular weight bigger hydrocarbons into low molecular weight smaller hydrocarbons by the application of heat, with or without a catalyst.

$$\underset{\text{Decane}}{C_{10}H_{22}} \xrightarrow{\text{cracking}} \underset{\text{n-pentane}}{C_5H_{12}} + \underset{\text{pentene}}{C_5H_{10}}$$

Nearly 50% of today's gasoline is obtained by cracking. It is important to note that the characteristics of gasoline obtained by cracking are far more superior to the straight run gasoline. The methods of cracking are summarized below

1. **Thermal cracking** When the heavy oils are subjected to high temperature and pressure in the absence of catalyst, it is called thermal cracking. The bigger hydrocarbons breakdown to give smaller molecules of paraffins, olefins and some hydrogen. This process may be carried out either in liquid phase or in vapour phase.

   (a) ***Liquid phase thermal cracking*** By this method any type of oil (residue, fuel oil or gasoline) can be cracked. The charge is kept in liquid form by applying high pressure of the range of 100 kg/cm^2 at a suitable temperature of 475–530°C. The cracked products are separated in a fractionating column. The octane rating of the product is 65–70

   (b) ***Vapour phase thermal cracking*** This method is suitable for oils which can be readily vaporised. The oil is first vaporised and then cracked at about 600–650°C and under a low pressure of 10–20 kg/cm^2. It requires less time than the liquid phase method. Petrol obtained from vapour phase cracking has better antiknock properties, but poorer stability than the petrol obtained from liquid–phase cracking.

Table 1.6 Comparison of liquid phase and vapour phase thermal cracking

Characteristic	**Liquid phase thermal cracking**	**Vapour phase thermal cracking**
Cracking temperature	475 – 530°C	600–650°C
Pressure	100 kg/cm^2	10–20 kg/cm^2
Octane rating of petrol	65–70	Greater than 70
Type of oil used for cracking	Any heavy oil can be cracked	Oil should be readily vapourised

2. **Catalytic cracking** It is carried out in the presence of a catalyst at a much lower temperature and pressure. The catalyst used is usually a mixture of silica and alumina (hydrated aluminium silicate) or zeolites in the form of beads or pellets.

   There are two main types of catalytic cracking

   (a) ***Fixed bed catalytic cracking*** The vapours of the oil are preheated in a pre-heater to a temperature of 420–450°C. It is then passed through a catalytic chamber containing either silica-alumina gel (SiO_2. Al_2O_3) or bauxite mixed with clay and zirconium oxide maintained at 425°C–450°C and 1.5 kg/cm^2 pressure. Cracking of heavy oil vapours takes place and 30–40% of the charge is converted into gasoline and about 3–4% carbon is formed which gets adsorbed on the catalyst bed. The cracked vapours then pass through a cooler where some gases are condensed along with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a 'stabilizer' where the dissolved gases are removed and pure gasoline is obtained.

After 8–10 h, the catalyst stops functioning because of the deposition of black layer of carbon formed during cracking. This is re-activated by burning off the deposited carbon. During the reactivation of the catalyst, the vapors of heavy oil are diverted through another standby catalytic chamber so that the reaction proceeds continuously.

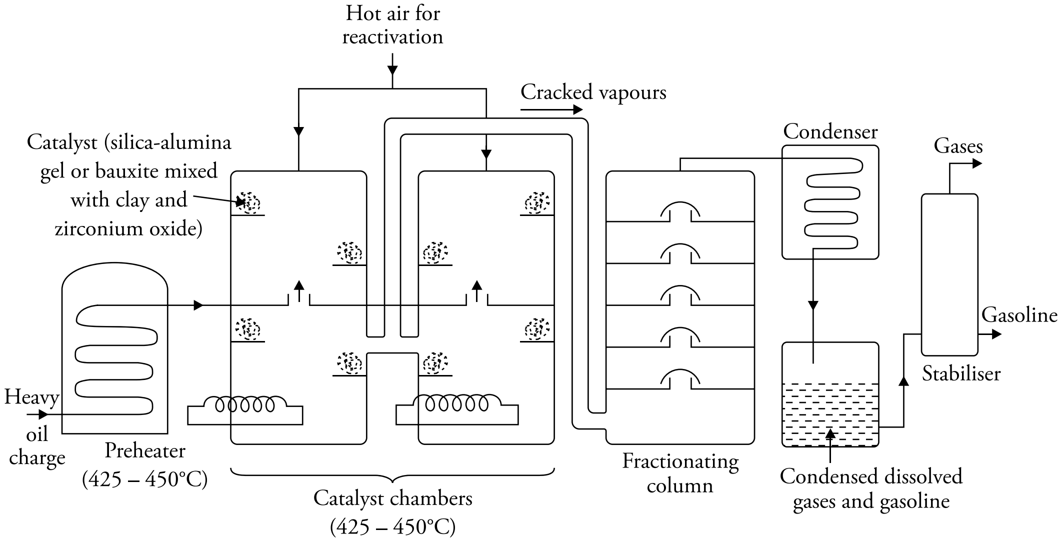


Figure 1.11 *Fixed bed catalytic cracking*

(b) ***Moving bed catalytic cracking*** This is also known as fluidized bed catalytic cracking. The feed oil is preheated. It is then mixed with powdered catalyst and the mixture of preheated heavy oil and powdered catalyst goes in a reactor maintained at 500°C. Cracking of heavy oil takes place. Near the top of the reactor there is a centrifugal separator (called cyclone) which allows the cracked vapours to pass on to the fractionating column but retains the catalyst powder. The catalyst powder gradually becomes heavier, due to coating with carbon formed and settles at the bottom. This is called *spent catalyst* and is forced by a blast of air to the regenerator maintained at 600°C. In regenerator carbon is burnt off and the catalyst is reactivated. The regenerated catalyst then flows through a standpipe to get mixed with fresh charge. The cyclone at the top of the regenerator allows the flue gases (CO_2, etc) to escape retaining the catalyst particles.

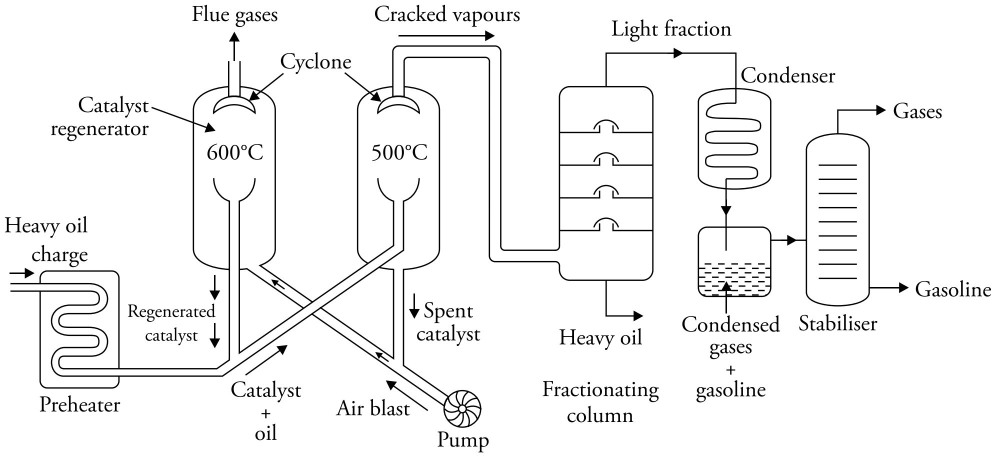


Figure 1.12 *Moving bed type catalytic cracking*

Advantages of catalytic cracking over thermal cracking

1. The yield of gasoline is higher. About 70% of the raw material by weight is converted into gasoline. The yield of gaseous products (byproduct gases such as alkanes and alkenes) is about 12–15% and only 4–6% of the raw material is converted into coke.
2. Production cost is low as high temperatures and pressures are not needed (pressure 1–5 kg/cm^2).
3. No external fuel is required for cracking since the heat required is obtained by burning the carbon deposited on the catalyst itself during regeneration process.
4. Process can be controlled to obtain desired products.
5. The percentage of gum or gum-forming compounds is very low.
6. The process is faster.
7. Action of catalysts is selective, hence cracking of only high-boiling hydrocarbons takes place.
8. The quality of gasoline produced is better because
   (i) The product contains very little amount of undesirable sulphur as the major portion of it escapes out as H_2S during cracking.
   (ii) The gasoline obtained by cracking contains low percentage of olefins and higher percentage of isoparaffin and aromatic hydrocarbons. This increases the antiknock properties of gasoline. Gasoline formed by catalytic cracking has an octane number of 80.

Decomposition of aromatics removes only side chains but the aromatic ring is not broken.

Synthetic petrol

Petrol can be synthesized by the following methods

1. ***Polymerization*** In this method small molecules of hydrocarbons are combined to form heavier molecules resembling gasoline.

   During cracking large quantities of olefins or unsaturated hydrocarbons (such as ethylene, propene and butene) and alkanes (such as methane, ethane, and butane) are obtained as by products. When this gaseous mixture is subjected to high pressure and temperature, with or without a catalyst, it polymerizes to form higher hydrocarbons resembling gasoline.

   The gasoline so obtained is called polymer gasoline. It has high octane number (78 to 83). Polymerization is carried out in two ways

   (i) ***Thermal polymerization*** In this the polymerization of cracked gases is carried out at 500–600°C and 70–350 kg /cm^2 pressure. The product is gasoline and gas oil which are separated by fractional distillation.

   (ii) ***Catalytic polymerization*** It is carried out in the presence of catalyst like phosphoric acid, sulphuric acid, etc. The process is carried out at a low temperature (150–200°C)

2. **Alkylation** This method is used to convert olefins to gasoline. In this process, alkane and alkene are combined together in the presence of a catalyst under proper temperature and pressure. The most important example is the reaction of isobutane and isobutene in the presence of anhydrous HF at room temperature to give isooctane. This process is used to produce gasoline of improved quality.

Conversion of coal into liquid fuels

Coal can be converted into gasoline by two methods:

(a) **Fischer Tropsch method** This method was developed by Fischer and Tropsch in 1962 in Germany. In this method the raw material is coke which is converted into water gas ($CO + H_2$) by passing steam over red-hot coke.

$$C + H_2O \xrightarrow{1200°C} \underset{\text{Water gas}}{CO + H_2}$$

A mixture of water gas and hydrogen is purified by passing through Fe_2O_3 (to remove H_2S) and then through a mixture of $Fe_2O_3 + Na_2CO_3$ (to remove organic sulphur compounds).

The purified gas is compressed to 5–25 atm. and then passed through a catalytic converter maintained at about 200–300°C. The catalyst consists of a mixture of

Cobalt (100 parts),Thoria (5 parts), Magnesia (8 parts) and Keiselguhr earth (200parts)

A mixture of saturated and unsaturated hydrocarbons is formed.

$$n\,CO + 2n\,H_2 \rightarrow C_nH_{2n} + H_2O$$

$$n\,CO + (2n + 1)H_2 \rightarrow C_n\,H_{2n+2} + n\,H_2O.$$

The reactions leading to the formation of hydrocarbons are all exothermic. The vapors coming out of the reaction chamber are passed through the cooler where liquid resembling crude oil is obtained. This is then subjected to fractional distillation to yield gasoline, diesel oil and heavy oil. The heavy oil can be reused for cracking to obtain more gasoline.

The gasoline formed by Fischer Tropsch process is rich in straight chain hydrocarbons, and hence its octane number is only 40. However, the diesel oil obtained is of excellent quality.

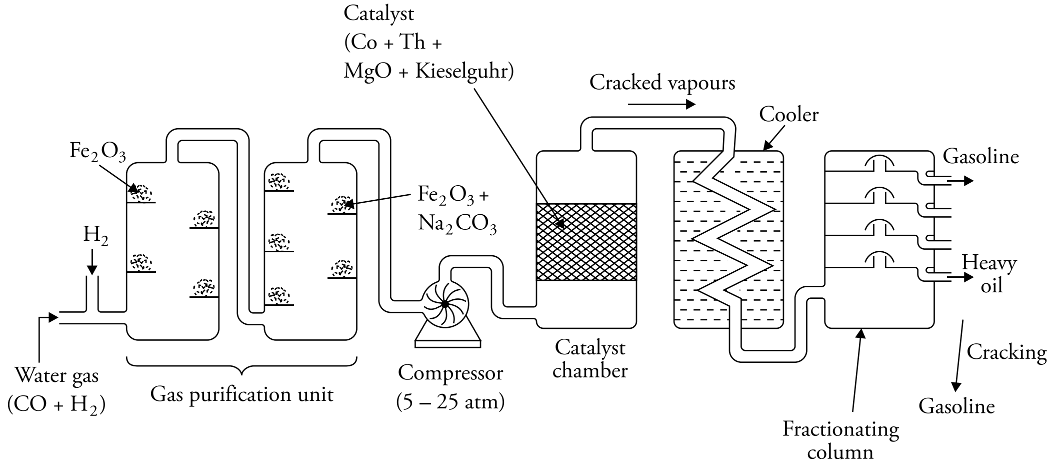


Figure 1.13 *Fischer - Tropsch method*

(b) **Bergius process**

This process developed by Bergius of Germany involves the conversion of low-grade coals, such as bituminous coals or brown coals, into liquid and gaseous fuels by hydrogenating them in the presence of catalyst.

In this process, the low ash coal is powdered and mixed with heavy oil and catalyst (tin and Ni oleate) to make a paste. This paste is heated with hydrogen at 450°C and 200–250 atm pressure for about 2 hrs. The coal undergoes hydrogenation to form saturated hydrocarbons that decompose at prevailing high temperature and pressure to yield low-boiling liquid hydrocarbons. The vapors leaving the catalytic chamber are condensed, where a liquid resembling crude oil is obtained. This is subjected to fractional distillation to give (i) gasoline, (ii) middle oil and (iii) heavy oil.

The middle oil is again hydrogenated to obtain gasoline. Heavy oil is reused for making a paste with fresh coal dust.

The gasoline so obtained contains 74% paraffins, 22% aromatics and 4% olefins. Yield of gasoline is about 60% of the coal dust used.

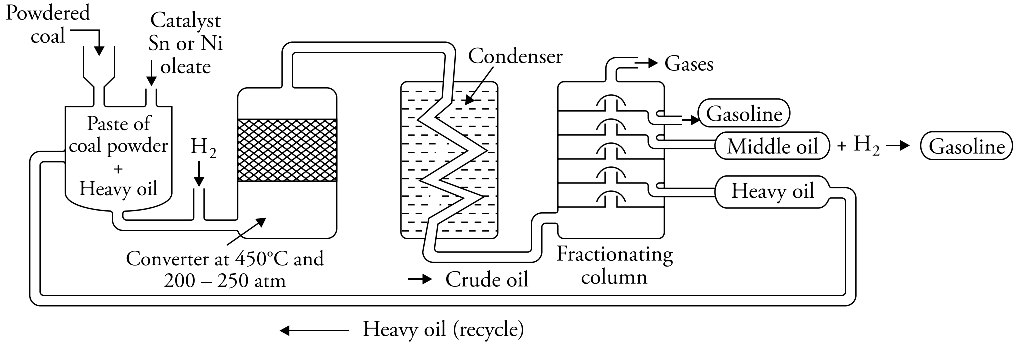


Figure 1.14 *Bergius process of hydrogenation of coal to gasoline*

Refining of gasoline

The straight run gasoline obtained from fractionation of crude petroleum or by synthesis contains substances such as (i) unsaturated olefins and (ii) sulphur. These substances are undesirable because

- Olefins undergo oxidation and polymerization leading to gum and sludge formation. These deposit on the walls of the carburetor and stop the engine.
- The sulphur compounds lead to corrosion of internal combustion engine. Moreover, compounds of sulphur such as mercaptans or H_2S have objectionable odors and make the oil sour.

Hence it has to be refined by chemical treatment.

(a) ***Removal of sulphur compounds*** The sulphur-containing gasoline is termed as sour gasoline and the process of removal of sulphur is called "sweetening". It is accomplished by treating gasoline with sodium plumbite with controlled addition of sulphur. The sulphur compounds are converted into PbS (removed by filtration)and disulphides (which are extracted with a suitable solvent). The above process is termed as ***Doctors process.***

$$Na_2PbO_2 + 2RSH \rightarrow Pb(SR)_2 + 2NaOH$$

$$Pb(SR)_2 + S \rightarrow \underset{\text{Lead sulphide}}{PbS(s)} + \underset{\text{disulphide}}{RSSR}$$

(b) ***Removal of olefins*** They are removed by percolating gasoline through fuller's earth which preferentially absorbs colours and olefins.

(c) ***Stabilization of gasoline*** Impure gasoline may contain dissolved gases such as methane, ethane, propane and butane. The process of removal of these impurities is called stabilization. For this, impure gasoline is passed through a fractionating tower having plates. The lower plates are heated with steam and are introduced near the upper plates. The stabilized gasoline is removed from the top of the column.

(d) ***Blending*** Purified gasoline is blended with high octane number fractions.

(e) ***Addition of inhibitors*** After refining, some inhibitors such as aromatic amines and aminophenols are added. These retard the oxidation process and prevent gum formation during storage.

(f) ***Doping*** In order to improve the antiknocking properties, tetraethyllead (TEL) is added. This is called doping

Characteristics of ideal gasoline

1. It must be cheap and readily available.
2. It must have a high calorific value.
3. It should be stable in storage. It should not form solid or gummy products on standing.
4. On combustion it should not cause corrosion in the engine. It should be free from water, sulphur compounds and other corrosion producing constituents.
5. It must be knock resistant and should have high octane number.
6. It should burn clean and should leave little carbon deposit during combustion.
7. It should have proper and partial vaporization on mixing with air in internal combustion engines. If it does not vaporize there will be difficulty in starting the engine. On the other hand if the volatility of gasoline is too high, it leads to vapour formation in the fuel line causing vapour locking. This reduces the fuel supply and the engine stops.
8. It should not pre ignite easily.
9. It should not tend to decrease the volumetric efficiency of the engine.
10. It should have a high specific gravity where there is a space limitation such as in aviation applications.

Knocking

It is defined as the metallic sound similar to rattling of hammer produced in internal combustion engine due to immature ignition of fuel air mixture.

An internal combustion engine uses either gasoline or diesel as fuel. In internal combustion engine, a mixture of fuel (gasoline or diesel) is ignited in a cylinder. The ignition is brought about by means of an electric spark (in petrol engines) or by compressing the air (in diesel engines).

The gases evolved during ignition, force the piston down due to high pressure thus producing the power stroke.

In a petrol engine the whole process comprises of four strokes;

(i) ***Suction stroke*** The downward moving piston sucks a mixture of air and petrol vapours in the carburetor into the cylinder.

(ii) ***Compression stroke*** The piston moves up, compressing the gas mixture. The ratio of initial volume (volume at suction stroke) to final volume (volume at compression stroke) is called compression ratio. It is here that a low octane rating fuel might ignite and cause knocking.

(iii) ***Power stroke*** Just before the piston reaches the top centre of the cylinder a spark from the spark plug ignites the gas mixture. The hot gases produced due to combustion increase the pressure and push the piston down.

(iv) ***Exhaust Stroke*** This is the last stroke in which the piston rises up and expels the exhaust gases from the cylinder.

The cycle then repeats itself**.** After the reaction is initiated by a spark, the fuel air mixture should burn smoothly and rapidly so that the expanding gas drives the piston down the cylinder smoothly.

Figure (1.15) represents schematic diagram of a four-stroke spark-ignition engine.

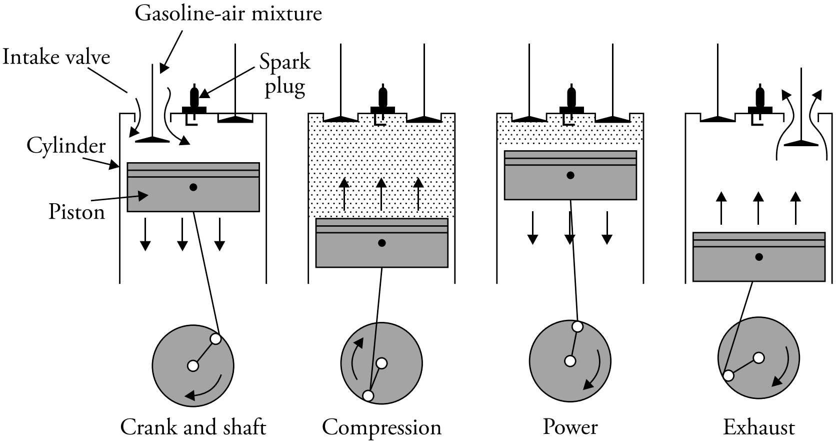


Figure 1.15 *Schematic diagram of a four-stroke, spark-ignition engine*

The efficiency of internal combustion engine depends on the compression ratio. Higher the compression ratio greater is the efficiency of the engine. To achieve maximum efficiency, a compression ratio of about 7–8 is required. However, if the compression ratio exceeds a certain limit, the fuel–air mixture may get heated to a temperature greater than its ignition temperature and spontaneous combustion of the fuel occurs even before sparking. This is called ***pre-ignition***. As a result of pre-ignition, the unburned fuel air mixture gets heated to such an extent that some of the hydrocarbons reach their ignition temperature and ignite all at once – explosively causing a metallic sound called ***knocking.***

Knocking decreases the efficiency of the engine and causes huge loss of energy and damage to piston and cylinder. Knocking depends on the chemical composition of the fuel, engine design, shape of head, location of plug, ports, etc, and also upon the running conditions.

Chemical structure and knocking

1. The knocking tendency decreases with increase in compactness of the molecule.
2. Knocking decreases with the increase in the number of double bonds and rings (cyclic structure).
3. With normal paraffins, the knocking increases with increase in length of the hydrocarbon chain. Thus, the knocking tendency increases from n-butane to n-heptane.

n-butane < n-pentane < n-hexane < n-heptane

———— knocking increases ————→

4. Knocking decreases as the branching in carbon chain increases.

   n-heptane > 2-methylhexane > 2, 2-dimethylpentane

   ———— knocking decreases ————→

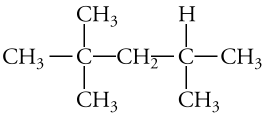
5. Aromatics such as benzene and toluene have very high antiknock properties.

   In general the tendency of fuel constituents to knock is in the following order

   Straight chain paraffins > branched chain paraffins (i.e., isoparaffins) olefins > cycloparaffins (i.e., naphthalenes) > aromatics.

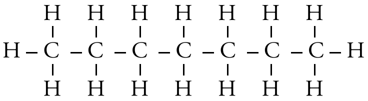
Octane rating

In order to classify the fuels according to their knocking property, an arbitrary scale was provided by Edger in 1926, known as octane rating or octane number. It is observed that n-heptane knocks very badly; hence, it was arbitrarily assigned an antiknock value of zero. On the other hand, isooctane (2,2,4-trimethylpentane) has a high resistance to knocking and hence was arbitrarily assigned a value of 100.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{H}{C}}-CH_3$$

Isooctane
2,2,4-trimethylpentane
(Octane number 100)



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

n-heptane
(Octane number 0)

Octane number of a fuel is defined as the percentage of isooctane in a mixture of isooctane and n-heptane, which has the same knocking characteristics as that of the fuel under examination, under same set of conditions. Thus, a fuel with octane number 80 is one which has the same combustion characteristics as a 80:20 mixture of isooctane and n-heptane.

Antiknocking agents Octane number of gasoline can be increased by addition of additives like benzol and alcohol. This process is called “blending”.

The antiknock properties of gasoline are usually increased by adding tetraethyl lead (TEL) $Pb(C_2H_5)_4$ and the process is called “doping”. TEL is a colourless liquid with a sweet odour but it is highly poisonous. About 0.5 ml of TEL per litre is added for motor fuels and about 1 ml of TEL per litre is added for aviation fuel. Gasoline containing TEL is coloured with 2% red dye to indicate its poisonous nature.

It is believed that knocking is a free radical mechanism. During combustion $Pb(C_2H_5)_4$ forms Pb and PbO. These act as free radical chain inhibitors and hence the propagation of the chain reaction leading to knocking does not take place.

However lead and lead oxide vapours so formed contaminate the atmosphere. Lead oxide is rapidly reduced to metallic lead which is deposited on the spark plug, cylinder walls and piston head. Hence, it is harmful to the engine. In order to solve these problems ethylene dibromide

($C_2H_4Br_2$) is also added, so that lead formed is converted into lead bromide, which is volatile and escapes into the atmosphere.

$$Pb + C_2H_4Br_2 \rightarrow PbBr_2 + CH_2{=}CH_2$$

Owing to harmful effects of lead, these days *unleaded petrol* is being used.

Unleaded Petrol It is one where octane number is increased without the addition of lead compounds. High octane number compounds such as isopentane, isooctane, ethylbenzene, isopropyl benzene, methyl tertiary butyl ether (MTBE) are used. Out of these, MTBE is preferred because it contains oxygen in the form of ether group and supplies oxygen for the combustion of petrol in internal combustion engines, thereby reducing peroxy compound formation.

Use of unleaded petrol requires the use of catalytic converter. A catalytic converter contains a catalyst (rhodium), which converts the toxic gases (CO and NO) to harmless gases (CO_2 and N_2, respectively). Moreover, it oxidizes unburnt hydrocarbon into CO_2 and H_2O.

Diesel engine fuels

In a diesel engine, the fuel is ignited not by a spark (as in petrol engine), but by the application of heat and pressure. The combustion cycle has four strokes

(i) ***Suction Stroke*** In this the air is drawn into the cylinder.

(ii) ***Compression Stroke***: Here, the air is compressed to a pressure of 30–50 kg/cm^2. Compression leads to rise in temperature to about 500°C.

(iii) ***Power Stroke*** Towards the end of compression stroke i.e., when the piston reaches its top centre (top centre is the moment when the piston has travelled into the cylinder as far as it can go and the compression is at its maximum), the diesel oil is injected in the form of fine droplets into the very hot compressed air. The fine particles of fuel absorb heat from the compressed air (at about 500°C) and ignite. The pressure of the gases evolved during the ignition/combustion pushes the piston downwards.

(iv) ***Exhaust Stroke*** This is the last stage of the cycle. In this the expulsion of hot gases from the cylinder takes place.

Knocking in diesel engine

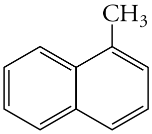
Ideally, ignition in diesel engine should begin just as the piston reaches the top center. When this does not happen, there occurs a time lag between injection of fuel and its ignition. *This interval between the start of fuel injection and its ignition is termed as ignition delay or induction delay.* It is obvious that for the efficient functioning of the diesel engine, this induction lag should be as brief as possible.

When a fuel has long induction lag a portion of the injected fuel gets accumulated in the cylinder even before ignition and when ignition takes place, the accumulated fuel burns violently leading to sudden increase in temperature and pressure. This non-uniform burning of the fuel is known as *diesel knocking*. The greater is the induction lag, higher is the diesel knock.

Chemically, diesel engine fuels consist of straight chain hydrocarbons with minimum amount of branched chain and aromatic hydrocarbons. Thus, in contrast to gasoline, the diesel engine fuel should have low spontaneous ignition temperature so as to minimize the induction lag.

Cetane Rating/Cetane number Cetane number is a measure of ignition quality of a diesel fuel. It is often mistaken as a measure of the fuel quality. It is actually a measure of the fuel's ignition delay. It is the measure of the ease with which the fuel will ignite under compression. The hydrocarbon Cetane (n-hexadecane) has a very short ignition delay as compared to any diesel fuel and is assigned an arbitrary value of 100. α-methyl naphthalene has a long ignition delay compared to any other diesel fuel and hence is assigned a value of 0 (zero).

$CH_3\text{-}(CH_2)_{14}\text{-}CH_3$
Cetane
or
n-hexadecane
(Cetane no. = 100)



α – methylnaphthalene
(Cetane no =0)

The cetane number of a diesel fuel is defined as the percentage of cetane (n-hexadecane) in a mixture of cetane and α*- methylnaphthalene, which will have the same ignition characteristics as the fuel under test, under the same conditions.* For example, a diesel fuel will be assigned a cetane number of 60 if it has the same ignition characteristics as that of a mixture of 60% cetane (n-hexadecane) and 40% α-methylnaphthalene. The cetane value of a fuel depends upon the nature and composition of hydrocarbon. The straight chain hydrocarbons ignite quite readily, although aromatics do not ignite easily. Ignition quality order among the constituents of diesel engine fuels in order of decreasing cetane number is as follows:

n-alkanes > naphthalene > alkenes > branched alkanes > aromatics

Thus, hydrocarbons which are poor gasoline fuels are quite good diesel fuels.

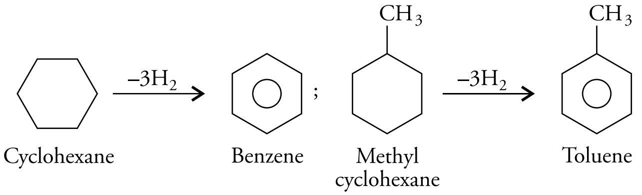
The cetane number of a diesel fuel can be raised by addition of small quantity of certain "pre –ignition dopes" such as ethylnitrite, isoamyl nitrite, acetone peroxide etc.

High-speed and Low speed diesel In a high-speed diesel engine the time lag in getting the diesel droplets heated to ignition point is very small, about 1/500th of a second. Such diesel engines require diesel with cetane number in excess of 45 (up to 60). On the other hand, low speed diesel requires a cetane number of about 25. Cetane number of medium speed diesel is about 35.

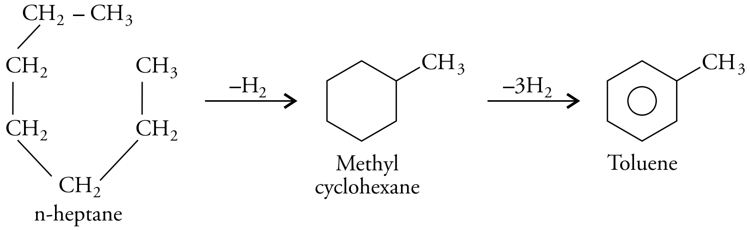
Reforming

Reforming is the process of improving the antiknocking characteristics of gasoline by bringing about certain structural modifications in it. The modifications are due to the rearrangement of molecules without disturbing their average molecular weight. The main reactions involved in reforming process are

(i) ***Dehydrogenation*** (removal of hydrogen)



(ii) ***Dehydrocyclization*** (Removal of hydrogen followed by cyclization)

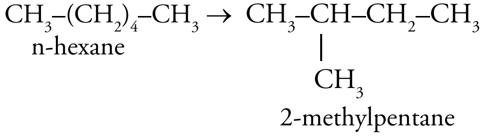


Hydrocracking (Breaking of the molecule in presence of H_2)

$$CH_3–(CH_2)_8–CH_3 + H_2 \xrightarrow{[Pt]} 2CH_3–(CH_2)_3–CH_3$$

n-decane n-pentane

Isomerization



$$\underset{\text{n-hexane}}{CH_3–(CH_2)_4–CH_3} \rightarrow \underset{\text{2-methylpentane}}{CH_3–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_2–CH_3}$$

Reforming can be carried out either thermally or in the presence of a catalyst.

Thermal Reforming In this process, the straight run gasolines are heated to a temperature of 500 – 600°C to a pressure of about 85 kg/cm^2. The degree of reforming is controlled by rapid cooling (quenching) with an oil spray. The reformed products are fractionated to remove residual gases. Alkanes and alkenes formed due to cracking may undergo dehydrogenation and cyclization to form naphthalenes. n-alkanes may also get converted into branched chain hydrocarbons (isomerization).

Catalytic reforming Catalytic reforming is carried out in the presence of a catalyst (platinum supported on alumina). It is carried out at 460 –530°C and a pressure of 35 –51 kg/cm^2. It can be either fixed bed or fluidized bed.

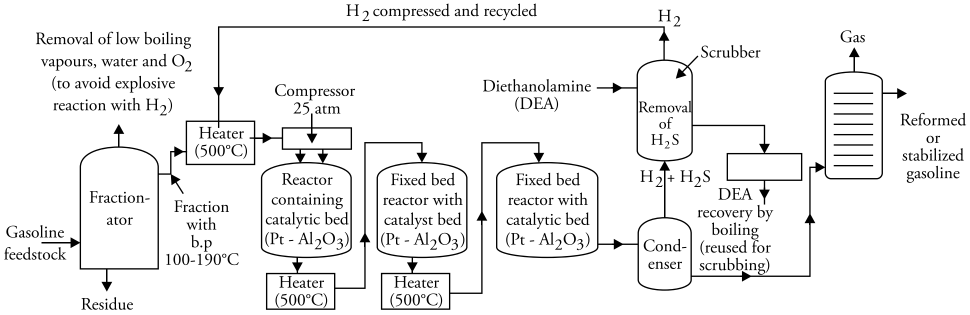


Figure 1.16 *Catalytic reforming*

Water, low boiling vapours, and oxygen are removed from the feedstock by heating and fractionation. This is done to avoid any explosive reaction with hydrogen. Out of different fractions obtained by fractionation, the fraction with boiling point 100–190°C is selected and mixed with compressed hydrogen. This mixture is heated upto 500°C by passing through a heater and is then compressed to 25 atm. The mixture is then passed through a series of three reactors, each containing Pt-Al_2O_3 catalyst bed.

As reforming is an endothermic process, hence the vapours have to be preheated before passing them from one reactor to the other. The products are condensed and separated into liquid and gaseous phase (consisting of H_2 and H_2S). H_2S is derived from sulphur compounds present in gasoline. It is removed by absorbing it in diethanolamine (DEA) in an H_2S scrubber. Part of H_2 formed is recycled for removing S in feedstock as H_2S and remaining is used for other purposes like hydrogenation of alkenes and hydrocracking. DEA can be regenerated by boiling and can be reused for scrubbing. The residue from the condenser is fractionated to remove the gases and higher boiling fractions.

Non petroleum fuels, power alcohol and aviation fuel

(a) **Benzol** It contains 70% benzene, 18% toluene and 6% xylene and rest other hydrocarbons and is obtained during the fractional distillation of light oil in the temperature range 80–170°C. Calorific value is 10200 kcal/kg and has an octane value of 87-90. It serves as a good fuel for internal combustion engines but cannot be used in cold countries as its freezing point is 55°C. It is generally used a blending agent with gasoline.

(b) **Power alcohol** Power alcohol is a mixture of 5–25% ethyl alcohol with petrol and is used as a fuel in the internal combustion engines. Ethyl alcohol with an octane number of 90 has good antiknocking properties, whereas the octane number of petrol is just 60–70. Thus, blending petrol with ethyl alcohol improves the antiknocking properties and octane number of the former and reduces carbon monoxide emissions from the engine. Ethyl alcohol absorbs traces of moisture present in the petrol.

Inspite of all these advantages use of ethyl alcohol is not very common because

- Its calorific value (7000 Kcal/kg) is much lesser than the calorific value of petrol (11500 Kcal/kg). Hence, addition of ethyl alcohol to petrol reduces its calorific value by 35%.

- Its surface tension is high and it is difficult to atomize it at lower temperature. This leads to starting trouble in a vehicle and the vehicle remains sluggish for quite some time after starting.
- Ethyl alcohol oxidizes into acid, causing corrosion of the engine parts.

(c) **Aviation fuels** The fuels used in spacecraft and aircrafts should be compact, light weight, occupy less space and produce more energy.

Aircrafts use special type of petroleum-based fuels, which are of a higher quality than those used in road transport. The fuels are blended with thousands of chemicals such as antioxidants, flame retardants that improve their performance and reduce the risk of explosion because of high temperature.

The fuels used in rocket help in their propulsion. They are combustible substances that burn to produce hot gases that eject out at a nozzle and help to propel the rocket or spacecraft in the forward direction. The fuels used consist of a substance that burns (fuels), a substance that assists burning (an oxidizer), certain metallic additives and performance improvers. The propellants used can be solid propellants, liquid propellants or hybrid propellants.

In solid propellants, the fuel is generally hydroxy-terminated polybutadiene (HTPB). Any one of the following oxidizers such as ammonium perchlorate, potassium perchlorate, ammonium nitrate, potassium nitrate or even cyclotrimethylene trinitramine (RDX) can be used. Powders of certain metals such as aluminium, magnesium and beryllium are also added. It may be noted that substances such as RDX act both as fuel and as oxidizer; nitrocellulose acts as a fuel, oxidizer and a plasticizer, whereas gunpowder uses charcoal as a fuel and potassium nitrate as the oxidizer, sulphur is added as a catalyst, although it participates in the reaction. One of the most commonly used solid propellants has the composition

Ammonium perchlorate 70%, aluminium 16%, elastomer polymer binder (polybutadiene, polyurethane) 14%.

Solid propellants are easier to store, handle and transport.

Spacecrafts also use liquid propellants such as nitrogen tetraoxide, hydrazine, hydrogen peroxide, etc. Liquid propellants are introduced into the combustion chamber of the spacecrafts as liquids. Their storage and transportation are rather difficult.

Hybrid propellants with solid fuel and liquid or gaseous oxidizers are also used in spacecraft.

1.7 Gaseous Fuels

Gaseous fuels can be obtained in many ways

(a) ***From nature*** Examples include natural gas and methane from coal mines.

(b) ***From solid fuels*** Examples include producer gas, water gas, coal gas and blast furnace gas.

(c) ***From petroleum*** Examples include refinery gases, LPG and gases from oil gasification.

(d) ***By fermentation of organic wastes*** Examples include biogas.

Natural gas

Natural gas is generally found to be associated with petroleum in nature and occurs near coal mines or oil fields. It is used not only as a fuel for domestic and industrial purposes but also as a raw material in various chemical syntheses. Natural gas that is derived from oil wells may be dry or wet. When natural gas is found to be associated with petroleum in oil wells, it is called 'wet gas'. It is obtained from the oil-producing wells and is a mixture of methane and higher hydrocarbons such as n-propane, n-butane, isobutane, isopentane, etc. When natural gas is found to be associated with crude oil, it is termed as 'dry gas'. It contains mainly methane and ethane with small amounts of CO, CO_2, H_2, H_2S, N_2 and inert gas. Wet natural gas has a higher calorific value than the dry gas because of the higher percentage of heavier unsaturated molecules.

The approximate composition of natural gas is

$$CH_4 = 70\text{–}90\ \%;\ C_2H_6 = 5\text{–}10\%;\ H_2 = 3\%;\ \text{Remaining CO and } CO_2.$$

Its calorific value varies from 12000 to 14000 Kcal/m^3.

Natural gas has wide ranging applications. It finds its use as a fuel in domestic and industrial sectors as well as in motor vehicles. It is also used to prepare ethane, propane, butane, acetic acid, etc. It serves as an important ingredient in the manufacture of various fertilizers, plastics, pharmaceuticals, fabrics and antifreeze agents.

Compressed natural gas (CNG)

It is obtained by compressing natural gas to a high pressure of about 1000 atmospheres. These days CNG is used as substitute for petrol and diesel. It is very economical and a clean fuel. It is better than LPG and is preferred over gasoline or LPG because-

- It is safer than gasoline or diesel because its ignition temperature is higher than gasoline or diesel.
- It is lighter than air and disperses easily in air, minimizing the risk of ignition. LPG being heavier than air settles at the ground level and hence is risky.
- As compared to gasoline, CNG produces lesser carbon monoxide on combustion.
- CNG-operated vehicles do not emit forbidden pollutants such as smoke, SO_2, SO_3, C_6H_6, HCHO etc.

LPG as a fuel

Liquified petroleum gas (LPG) is commonly used as a domestic fuel, industrial fuel and a fuel in motor vehicles. Chemically, it is a mixture of C_3 and C_4 hydrocarbons of the corresponding alkane and alkene series. It is generally obtained as a byproduct during the cracking of heavy oils or from natural gas. The gas obtained by cracking is dehydrated, desulphurized and bottled in cylinders under high pressure. Highly odorous ethylmercaptan is added to it to detect leakage.

Composition LPG mainly contains paraffin hydrocarbons up to C_4 and its main constituents are n-butane, isobutane, butylene and propane with little or no propylene or ethane. These hydrocarbons exist in gaseous form under atmospheric pressure but can be liquified readily under pressure.

Properties

- It is a colourless, tasteless gas having very faint odour.
- It is 1.5 – 2.0 times heavier than air and can be easily liquefied at moderate pressure. The liquid is immediately transformed into vapour as soon as the pressure is released.
- It is non-toxic and non poisonous but being heavier than air it pushes the air out of the room and can lead to suffocation.
- It is inflammable and has a high calorific value of nearly 27800 Kcal/m^3. This is nearly three times the calorific value of natural gas and seven times that of coal gas.

Coal gas

It is obtained when coal is heated in the absence of air at about 1300°C in gas retort or coke ovens. The fuel used for the purpose is a mixture of producer gas and air.

$$\text{Coal} \xrightarrow[\text{in absence of air}]{1300^\circ\text{C}} \underset{\text{(Residue)}}{\text{Coke}} + \text{Coal gas} \uparrow$$

Tar, NH_3, naphthalene and benzene are removed by passing the outcoming gases through water, cold water, petroleum or creosote oil respectively. H_2S is removed by passing it over moist ferric oxide contained in a purifier (Fig. 1.17).

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O$$

When iron oxide is exhausted it is taken out from the purifier and exposed to air where it gets oxidized to ferric oxide.

$$2Fe_2S_3\,(s) + 9O_2\,(g) \rightarrow 2Fe_2O_3\,(s) + 6\,SO_2\,(g)$$

The purified coal gas is finally stored over water in gas holders.

Coal gas is a colorless gas having a characteristic odour. It is lighter than air and burns with a long smoky flame. Its average composition is

$$H_2 = 40\%;\ CH_4 = 32\%;\ CO = 7\%;\ C_2H_2 = 2\%;\ C_2H_4 = 3\%;\ N_2 = 4\%;\ CO_2 = 1\%.$$

Its calorific value is 4900 Kcal/m^3.

Uses

- As illuminant in cities and towns.
- As a fuel.
- As a raw material for ammonia production.
- In metallurgical operations for providing a reducing atmosphere.

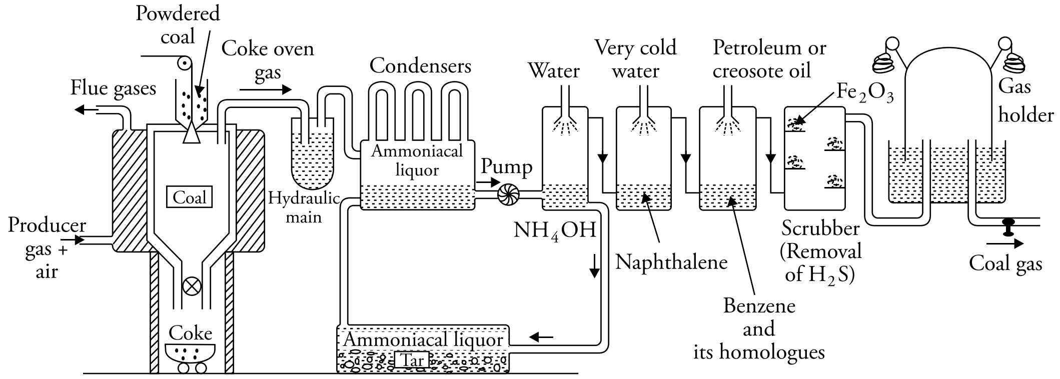


Figure 1.17 *Manufacture of coal gas*

Oil gas

It is obtained by the cracking of kerosene oil.

Production

The plant used for the purpose consists of a strong cast iron retort enclosed in a coal-fired furnace. A bonnet is fitted at the mouth of the retort through a water seal. A pipe from the hydraulic main leads to the gas holder. This pipe has a testing tap from where the samples of gas can be taken for testing (Fig. 1.18).

Working

The retort is heated to red hot and a stream of oil is continuously allowed to fall on the red-hot bottom of the retort. The oil on coming in contact with the red-hot bottom immediately gets cracked into a number of lower gaseous hydrocarbons.

$$C_{12}H_{26} \rightarrow CH_4 + C_2H_6 + C_2H_4 + C_2H_2 + C_3H_8 + C_3H_6 + C$$

Kerosene oil Mixture of Hydrocarbons Tar

The gaseous mixture so obtained passes through the bonnet to a hydraulic tank (tank containing water) where tar gets condensed. Then at the testing tap, proper cracking of the gas is estimated from the color of the gas. A good oil gas should have a golden color. By properly adjusting the supply of air, golden color is obtained. The gas is finally stored over water in gas holders.

The yield of gas is 40–50% and its calorific value is about 4500 – 5400 Kcal/m^3.

Approximate composition of oil gas

Constituent	Methane (CH_4)	Hydrogen (H_2)	Carbon monoxide (CO)	Carbon dioxide (CO_2)
Percentage	25–30%	50–55%	10–15%	3%

Applications

- It is used as laboratory gas.
- It is also used to improve the calorific value of water gas and the mixture of the two gases is called carbureted water gas.

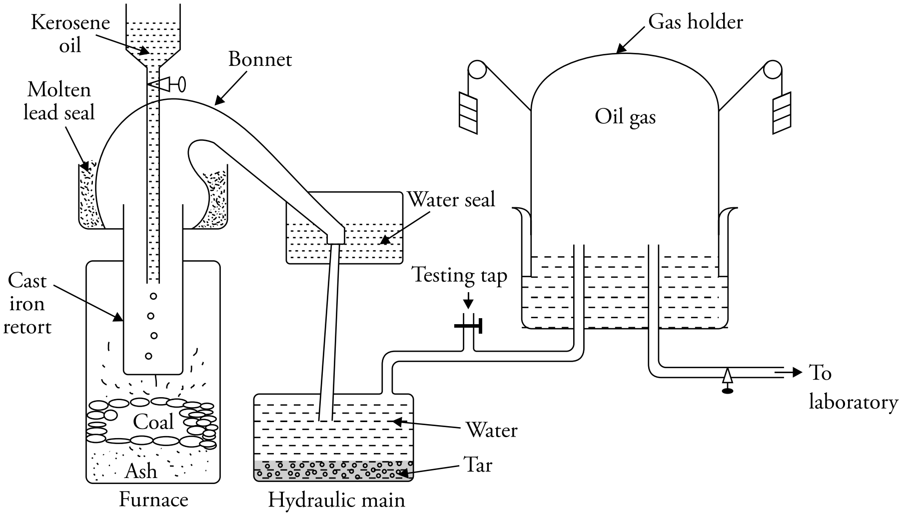


Figure 1.18 *Manufacture of oil gas*

Producer gas

It is a mixture of carbon monoxide (combustible gas) and nitrogen (non-combustible gas).

Preparation It is prepared by passing air mixed with a little steam (about 0.35 kg/kg of coal) over red hot coal or coke bed maintained at 1100°C in a special reactor called 'gas producer'. Gas producer is a steel vessel, about 3 m in diameter and 4 m in height. It is lined inside with refractory bricks to maintain a temperature of about 1100°C. At the top of the reactor there is a cup and cone arrangement for feeding the charge and a side opening for the exit of producer gas. At the base there is inlet for air and steam and an exit for the ash formed (Fig. 1.19).

Reaction When a mixture of air and steam is passed over red hot coke or coal bed at 1100°C in gas producer the following reactions take place in different zones of the fuel bed

(i) ***Ash Zone*** It is the lowest zone consisting mainly ash. It is about 0.8 m thick. The function of this zone is

  (a) To preheat the air and steam mixture as it passes through this zone
  (b) As ash is bad conductor of heat it protects the grate (metal framework at the base for holding fuel) from intense heat of combustion.

(ii) ***Combustion zone or oxidation zone*** It is the zone next to the ash zone. In this zone carbon of the coal or coke burns in the presence of air to form CO and CO_2. The temperature of this zone is about 1100°C.

$C + O_2 \rightarrow CO_2 + 97$ Kcal

$C + \frac{1}{2} O_2 \rightarrow CO + 29.5$ Kcal

(iii) ***Reduction Zone*** Here carbon dioxide (produced in combustion zone) and steam combines with red hot coke to liberate free hydrogen and carbon monoxide

$2C + O_2 \rightarrow 2CO - 36$ Kcal

$C + H_2O \rightarrow CO + H_2 - 29$ Kcal

$C + 2H_2O \rightarrow CO_2 + 2H_2 - 19$ Kcal

As all the above reactions are endothermic the temperature of this zone falls to 1000°C. For the production of producer gas only air can be used, however, usage of steam along with air is beneficial because

(a) It raises the content of combustible component ($CO + H_2$), thereby increasing the calorific value.

(b) The endothermic reaction of steam and carbon prevents the temperature from rising too high and prevents the fusion of ash and refractory lining.

4. ***Distillation Zone*** This is the uppermost part of the fuel bed. Here (400–800°C), the outgoing gases give a portion of their heat to the down coming coal. This along with heat radiated from the reduction zone helps to distil the fuel, thereby volatile matter of coal is removed and comes out with outgoing gas.

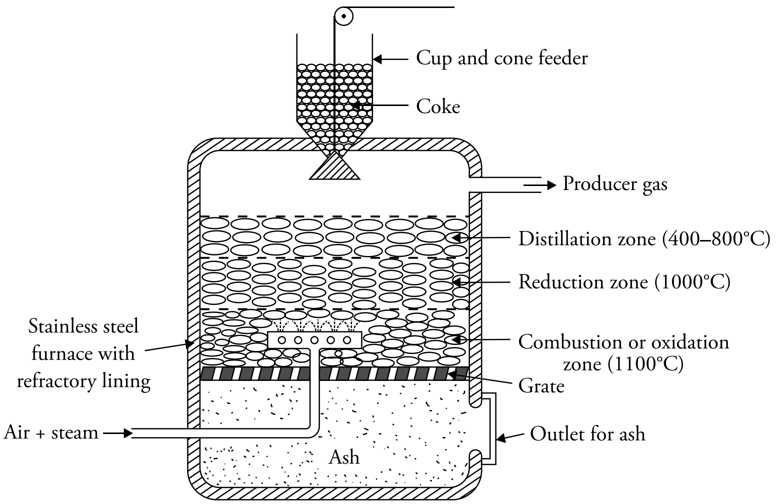


Figure 1.19 *Manufacture of producer gas*

Composition The average composition of producer gas is

	Combustible gases		Non-Combustible gases	
Constituent	CO	H_2	N_2	CO_2
Percentage	22–30 %	8–12 %	52–55 %	3%

It is insoluble in water and is poisonous in nature. Its calorific value is about 900–1300 Kcal/m^3

Applications

- As a reducing agent in metallurgical operations
- As a fuel for heating open- hearth furnaces, muffle furnace and retorts(used in coke and coal gas manufacture)

Water gas

It burns with a blue flame and is often termed as 'blue gas'. It is a mixture of carbon monoxide and hydrogen with little amount of non-combustible gases such as carbon dioxide and nitrogen. Its calorific value is nearly 2800 Kcal/m^3 and is prepared by passing steam over red hot coke at about 1000°C.

$$C + H_2O \rightarrow \underset{\text{Water gas}}{CO + H_2} \qquad \Delta H = +28 \text{ Kcal}$$

The above reaction being endothermic requires lot of heat to maintain the temperature of the furnace. If this heat is supplied from an external source the process would become uneconomical; hence, the reaction is carried out in two steps. In the first step air is blown to generate heat, and in the second step steam is blown and the formation of water gas takes place with the absorption of heat. These two steps are called *blow and run periods*, respectively.

Manufacture The gas generator is made up of steel with a refractory lining. It has a cup and cone arrangement at the top for feeding the coke. At the bottom it is provided with two separate inlets for steam and air supply. There is an outlet for the removal of ash at the bottom and for the exit of water gas near the top (Fig. 1.20).

The following reactions are involved

1. Air is passed through the coke bed when the carbon of the coke burns in the presence of the oxygen in air to produce carbondioxide. This reaction is exothermic and the temperature of the fuel bed rises to 1000°C. This is the *blow step* of the cyclic process.
2. When a sufficiently high temperature is attained the supply of air is cut off and then steam is blown through the red hot bed of coke. Steam combines with coke to form water gas

$$C + H_2O \rightarrow \underset{\text{Water gas}}{CO + H_2} \qquad \Delta H = +28 \text{ Kcal}$$

The second step is the *run step* of the cyclic process. This step is endothermic and hence the temperature again begins to drop. Again the supply of steam is stopped and air is supplied. The cycle is repeated alternately to maintain the required temperature.

Composition

The approximate composition of water gas is

H_2 = 51%; CO = 41%; N_2 = 4%; CO_2 = 4%

Uses

Water gas is used as a fuel in furnace; it is used in Fischer – Tropsch process for the manufacture of synthetic petrol. Its mixture with hydrogen is used for the manufacture of methanol.

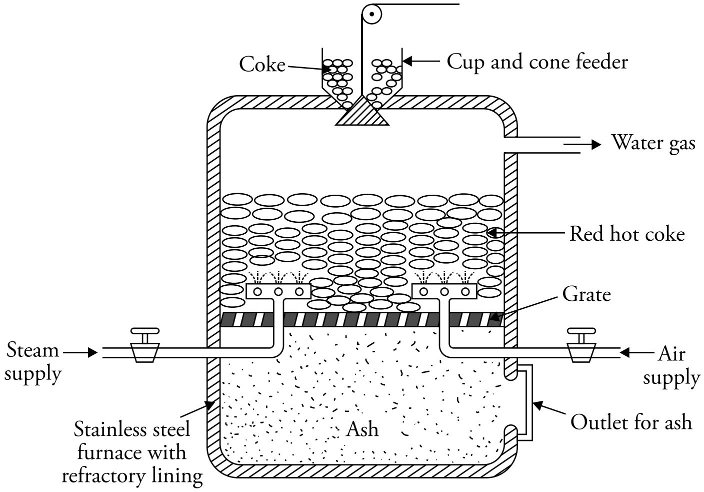


Figure 1.20 *Manufacture of water gas*

Carbureted water gas The calorific value of water gas is very low (2800 Kcal/m^3). Its calorific value can be increased by mixing it with gaseous hydrocarbons obtained by the cracking of crude oils. This enhances the calorific value of water gas to 4500 Kcal/m^3. The average composition of carbureted water gas is

CO = 23 – 28 %, H_2 = 34 – 38 %; Saturated and unsaturated hydrocarbons = 30 – 48 %;
CO_2 = 0.2 – 2.5 %; N_2 = 2.5 – 5 %

Biogas

Biogas is produced by the anaerobic decomposition of biological matter. Organic matter animal dung, poultry waste, vegetable matter, human excreta, plant wastes, etc are subjected to the action

of microorganisms in closed tank in the absence of oxygen (anaerobic conditions). The organic matter undergoes degradation and a gas rich in methane is evolved. This gas is collected and can be used in kitchens as a fuel. It is highly inflammable and is called biogas or *gobar* gas.
Its approximate composition is:

CH_4 = 55%; H_2 = 7.4 %; CO_2 = 35%; N_2 = 2.6 % and H_2O = traces.

Its average gross calorific value is 5300 Kcal/m^3

Manufacture A biogas plant consists of an underground tank called the digester and a gas holder above the ground. The digester is made up of bricks masonary wall in cement mortar. Two small tanks are constructed on the ground on either sides of the digester. In one tank the dung and water are mixed and fed into the digester by a sloping pipe. Another pipe serves as an outlet pipe through which the digested slurry is removed and collected in the second tank. A gas holder made up of steel is placed on top of the digester and it helps to collect the gas thus produced. It can be fixed or floating type (Fig. 1.21).

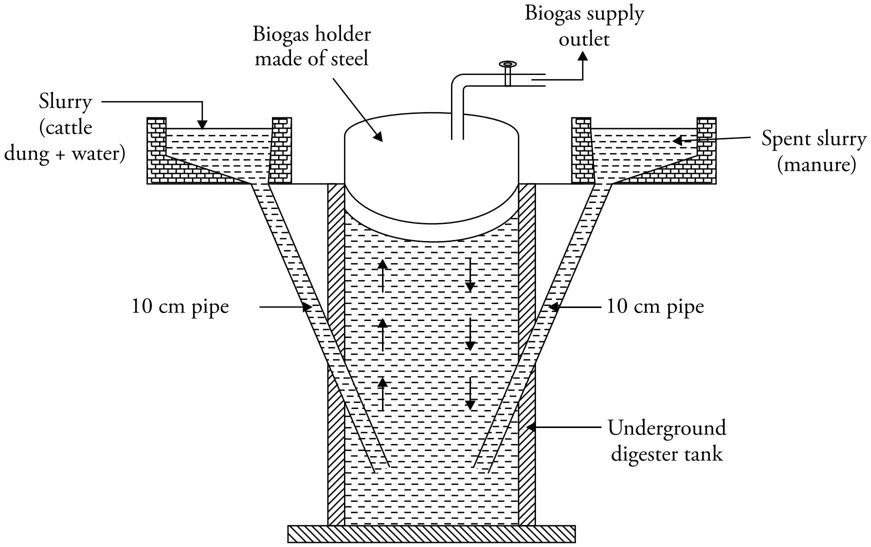


Figure 1.21 *Floating gas holder type biogas plant*

Working A mixture of animal dung and water in equal proportion (slurry) is fed into the digester with the help of the inlet pipe. The slurry is filled till the top of the digester. It undergoes fermentation in about 50 to 60 days, and the biogas starts accumulating in the dome-shaped gas holder. The pressure of the gas pushes the digested slurry out, which is collected in another tank and is used as a manure.

Uses Biogas is a clean fuel and is used for cooking and as an illuminant in rural areas. The spent slurry is a very useful fertilizer and has 43% more strength than dung used directly as manure.

1.8 Analysis of Flue Gas

The gaseous products formed after combustion of a fuel are called *flue gases*. The flue gases consist of carbon dioxide, sulphur dioxide, carbon monoxide, nitrogen, water vapor and excess oxygen.

For proper and efficient combustion of a fuel, it is essential that the fuel comes in contact with sufficient quantity of air to burn all the combustible matter present. The analysis of flue gases gives an idea about the complete or incomplete combustion process. The analysis is usually carried out to measure the amount of CO_2, CO, O_2 and N_2 in the flue gases. Thus,

1. If the analysis shows the presence of CO, it indicates the incomplete combustion of the fuel or shortage of oxygen. Hence, the supply of oxygen should be increased or the supply of fuel should be reduced.
2. If the flue gases contain a considerable amount of oxygen, it indicates that the combustion is complete but the supply of air is very much in excess. Ordinarily, 50–100% excess air is generally supplied but too much excess air results in loss of heat. In such cases, the supply of air is reduced or the rate of supply of fuel is increased.
3. If the analysis shows the presence of oxygen and carbon monoxide, it indicates that the combustion is irregular and non-uniform, i.e., in some parts of the furnace, there is excess air and in some other parts the supply of air is insufficient. Hence, the supply of air is to be regulated in all the parts of the furnace. The analysis of flue gases is carried out with the help of Orsat's apparatus.

Orsat Apparatus

Construction It consists of a horizontal tube having a three-way stop cock at one end and a graduated burette at other end. The free end of the stop cock is further connected to a U-tube containing fused $CaCl_2$ and glass wool (to remove moisture and smoke particles from the flue gas). The burette is surrounded by a water jacket to keep the temperature of the gas constant during the experiment. The lower end of the burette is connected to a water reservoir by means of a long rubber tubing. The level of water in the reservoir can be raised or lowered by raising or lowering the water reservoir (Fig. 1.22).

The horizontal tube is connected in series to a set of three absorption bulbs A, B and C each through a stop cock. The absorption bulbs are filled with glass tubes so that the surface area of contact between the gas and the solution is increased.

The absorption bulbs have solutions for the absorption of CO_2, O_2 and CO respectively.

- Bulb A contains KOH to absorb CO_2 (250 g KOH in 500 ml of boiled distilled water).
- Bulb B contains a solution of alkaline pyrogallic acid. (25 g of pyrogallic acid + 200 g KOH in 500 ml of distilled water).It can absorb CO_2 and O_2.
- Bulb C contains 'ammoniacal cuprous chloride solution. (100 g cuprous chloride +125 ml liquor ammonia + 375 ml of water). It can absorb CO, CO_2 and O_2.

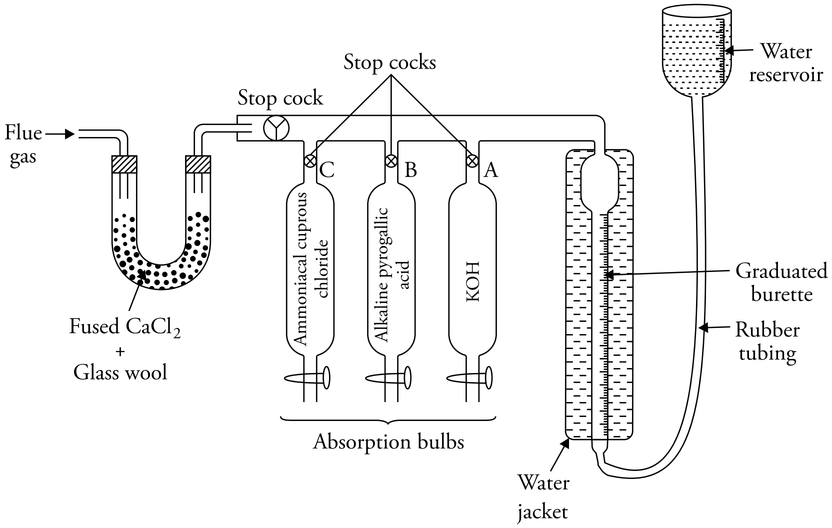


Figure 1.22 *Orsat's apparatus*

Working

(i) The whole apparatus is cleaned thoroughly. The stoppers are greased and are tested for their air tightness. The bulbs A,B and C are filled with their respective solutions and their stop cocks are closed. The jacket and leveling reservoir are filled with water.

(ii) The three-way stop cock is opened to atmosphere and the reservoir is raised till the burette is completely filled with water and air present in it is removed.

(iii) The three-way stop cock is now connected to the flue gas supply and the reservoir is lowered. The flue gas to be analyzed enters in after passing through the $CaCl_2$ U-tube which absorbs moisture present in the flue gas. However, this flue gas is mixed with air present in the apparatus and hence is expelled out by opening the three-way stop cock and raising the reservoir. This process is repeated 3–4 times to ensure complete removal of the air present in the apparatus.

(iv) Finally, the flue gas is sucked in the burette and the volume is adjusted to 100 ml at atmospheric pressure. This is done by adjusting the height of the leveling reservoir. The three-way stop cock is opened to the atmosphere and the reservoir is carefully raised, till the level of water in it is the same as in the burette which stands at 100 ml mark. The three way stop cock is then closed.

(v) Now the stopper of bulb A (containing KOH) is opened and the water reservoir is raised. The flue gas is again sent to the burette by lowering the reservoir. By raising the reservoir several times complete absorption of CO_2 is ensured. The unabsorbed gases are finally taken back to the burette, till the level of solution in the CO_2 absorption bulb stands at a constant mark. After this the stop cock is closed. The levels of water in the burette and reservoir are equalized and the volume of the residual gases is noted. The decrease in volume gives the volume of CO_2 in 100 ml of the flue gas sample.

(vi) Now the stop cock B is opened and the process is repeated as mentioned above. The decrease in volume gives the volume of O_2 in 100 ml of flue gas.

(vii) Similarly the flue gas is passed through the bulb C to determine the amount of CO.

(viii) The gas remaining in the burette after the absorption of CO_2, O_2 and CO is taken as nitrogen.

Precautions

1. The flue gases should be passed first in bulb A (KOH solution), then bulb B (pyrogallic acid solution) and then through bulb C (ammoniacal cuprous chloride solution) because KOH absorbs CO_2, pyrogallic acid absorbs $CO_2 + O_2$ and ammoniacal Cu_2Cl_2 absorbs $CO_2 + O_2 + CO$.
2. CO should be determined carefully as its amount is very small.
3. All the air should be expelled from the apparatus before starting the experiment.

1.9 Renewable Sources of Energy

The various energy sources such as coal, petrol, diesel discussed in the previous sections are derived by the fossilization of plant and animal remains that got buried under the earth millions of year ago. These resources are limited, and with the rapidly growing energy demand they are likely to be depleted soon. To meet the rising global energy demand it is essential to focus on energy resources that are inexhaustible and abundantly available. These energy sources are termed as renewable or non-conventional energy sources. The various non-conventional energy sources are

- Solar energy
- Wind energy
- Energy from water/ hydroenergy
- Energy from biomass
- Tidal and wave energy
- Ocean thermal energy conversion
- Geothermal energy
- Hydrogen energy

Solar energy Sun is the major source of energy on earth. It gives 1000 times more energy than we require. If this energy is trapped economically the energy crisis of the world would be solved. Solar energy can be used either

(i) Directly as thermal energy like in solar cookers, solar water heater, solar dryers, desalination of sea water, etc.

(ii) Indirectly using photovoltaic cells to convert solar energy to electricity. This is carried out by using silicon solar cells. The electricity so generated can be used for street lighting, lightning homes and buildings, running motors, pumps, electric appliances, etc.

Although the initial installation cost of a solar plant is high, it is clean energy, does not discharge harmful products in air and once installed the running cost is less and hence it is cheap.

Wind energy It is the power generated by harnessing the wind energy usually by windmills. To harness wind energy windmills are built. When the wind blows the blades rotate and by connecting the wind turbine to electric generator wind energy can be converted into electrical energy.

Wind energy, like solar energy is clean energy. The operation and maintenance cost of windmill is low. However, the initial installation cost is high.

The demerits include the uncertainity of the strength of wind, high noise created by the moving windmill; moreover it also affects scenic beauty of the natural landscape adversely. Sometimes birds are killed by flying into the rotors.

Energy from water/hydroenergy For this water is stored in dams and then allowed to flow through the tunnels on the turbines. This rotates the turbines, which then drives generators to produce electricity.

Hydroelectricity can be generated continuously without any type of pollution; however, building dams involves heavy investment. Dams also have adverse effect on the environment.

Energy from Biomass The organic matter like plants, agricultural waste, organic waste from industries and cities, municipal solid waste, forest residues constitutes the biomass which can be used to generate energy by either (i) Direct incineration or (ii) Anaerobic digestion.

In direct incineration the organic waste is burnt and the heat thus generated is used to boil water in boilers. This steam drives the turbine and generates electricity. In the process of anaerobic digestion the organic matter is decomposed anaerobically by bacteria. This produces gases (mainly methane) that are used for various purposes. *Gobar* gas used in households is produced by anaerobic digestion of cow dung, animal and human waste.

Tidal and wave energy Tidal energy is generated due to the difference in potential energy of water during high tide and low tide. The water rises to a maximum during high tide and falls to a minimum during low tide. To trap tidal energy a barrage or embankment is built across the sea. During high tide water is lifted and stored in the barrage which flows out from the reservoir into the sea through turbines coupled to electric generators.

Ocean thermal energy conversion (OTEC) A temperature difference exists between the surface and deep sea water. This temperature difference between the surface and deep sea water is utilized to generate electricity.

This process is based on the thermodynamic principle which states that if a heat source (warm ocean surface water)is available at a higher temperature and a heat sink (deep colder water) at a lower temperature then it is possible to utilize the temperature difference to convert part of the heat from the source into mechanical energy by connecting the turbine to a generator. The residual heat in discharged to the sink which is at a lower temperature.

Geothermal energy Geothermal energy is the energy which lies embedded within the earth's crust. The temperature of earth increases with depth below the surface. All the heat stored in the earth's crust as thermal energy constitutes an inexhaustible source of energy termed as geothermal energy.

Hot molten rock called 'magma' is present at a depth of 25–40 Km below the earth's surface. This molten magma is sometimes pushed up towards the surface resulting in volcanic action. When ground water comes in contact with magma it gets heated. In some places, the steam or hot water comes out of ground naturally through cracks in the form of natural geysers; this hot geothermal water or steam is used to operate turbines to generate electricity.

Hydrogen energy Hydrogen is often considered as a non-conventional fuel because it is produced from water which can be split into gaseous hydrogen and oxygen by an electrical process called electrolysis. Hydrogen can also be produced from natural gas and biomass resources.

Hydrogen is considered as a renewable fuel because the earth's supply of water is unlimited. Hydrogen gas can be used like natural gas. It can be burnt to heat buildings, cook food and produce electricity in power plants. Hydrogen can also be used as fuel in automobiles, in a jet aircraft (liquid hydrogen). Hydrogen can also be used in fuel cell devices that combine hydrogen and oxygen to produce electricity.

Advantages of renewable energy

1. One of the major advantages of renewable energy is that, as it is renewable, it is sustainable and will therefore never run out.
2. Renewable energy facilities require less maintenance than traditional generators.
3. As their fuel is derived from natural and available sources, the cost of operation is less.
4. Renewable energy produces little or no waste products such as carbondioxide or other chemical pollutants, so it has minimal impact on the environment.

Disadvantages of renewable energy

1. It is difficult to generate the quantities of electricity as large as that produced by traditional fossil fuel generators.
2. It can be unpredictable and inconsistent. The supply from renewable sources is not reliable, as it relies on weather for its source of power. Hydro generators need rain to fill dams, wind turbine needs wind to turn the blades and solar collectors need clear skies and sunshine to collect heat and generate electricity.
3. The current cost of renewable energy technology is far in excess of traditional energy. This is because it is a new technology and as such has extremely large capital cost.

1.10 Combustion Calculations

Combustion is a chemical reaction accompanied by the liberation of heat. It is an exothermic process. For example

$$C(s) + O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H = -97 \text{ Kcal.}$$

To ensure complete combustion of a fuel, it is essential that appropriate amount of oxygen and air is supplied. If the amount of oxygen and air supplied is insufficient, complete combustion will not take place and too much excess should also not be supplied.

Hence in any industrial and metallurgical processes it is essential to calculate the minimum amount of oxygen and air required for the complete combustion of the fuel used.

Calculation of air required for the combustion of solid and liquid fuels

The elements generally present in the fuel are carbon, hydrogen, oxygen, nitrogen and sulphur. During combustion of the fuel these elements combine with oxygen. If the percentage composition of fuel is known, the amount of oxygen required for combustion can be calculated. The method of calculation of air is summarized below

(i) Weight of each constituent present per kilogram of the fuel is calculated from the percentage composition of the fuel. Let the weight of carbon, hydrogen, oxygen, and sulphur in one kg of the fuel be C kg, H kg, O kg and S kg respectively.

(ii) The quantity of oxygen required for the combustion of C kg of carbon, H kg of hydrogen, S kg of sulphur can be calculated with the help of the equations given below

Combustion of carbon

$$\underset{12\text{kg}}{C} + \underset{32\text{ kg}}{O_2} \rightarrow CO_2$$

12 kg of carbon requires 32 kg of oxygen.

C kg of carbon requires $\frac{32}{12} \times$ C kg or 2.67 C kg of oxygen.

Combustion of hydrogen

$$\underset{2\text{kg}}{H_2} + \underset{16\text{kg}}{\frac{1}{2} O_2} \rightarrow H_2O$$

2 kg of hydrogen requires 16 kg of oxygen.

H kg of hydrogen requires $\frac{32}{12} \times$ H kg or 8H kg of oxygen

Combustion of sulphur

$$S + O_2 \rightarrow SO_2$$

32 kg of sulphur requires 32 kg of oxygen.

S kg of sulphur requires $\frac{32}{32} \times$ S kg or 1 S kg of oxygen.

The other constituents present in fuel do not require oxygen.

Thus, total quantity of oxygen required for the combustion of 1 kg of fuel will be

$$(2.67C + 8\ H + S)\ \text{kg}.$$

If oxygen is already present in the fuel, the quantity of oxygen to be supplied from air

(Total oxygen required–O_2 present in fuel)

$$(2.67C + 8\ H + S - O)\ kg$$

So, minimum quantity of O_2 or the theoretical amount of O_2 required for the complete combustion of 1 kg of a fuel

$$= (2.67\ C + 8\ H + S - O)\ kg$$

As air contains 23% oxygen by weight; hence, minimum weight of air required for combustion

$$= (2.67\ C + 8\ H + S - O)\ \frac{100}{23}\ kg.$$

Calculation of volume of oxygen or air required

At certain temperature and pressure, the mass of any gas can be converted into its volume and vice versa by using the gas equation. The volume of oxygen or air required for the combustion of fuel is calculated

$$PV = \frac{W}{M} \times RT$$

Where,

P = pressure of gas in atmosphere;	V = Volume of gas
R = gas constant;	T = temperature in K
W = mass of gas;	M = Molecular mass of the gas.

Alternatively the weight of oxygen required can be converted into its volume at normal temperature and pressure. 22.4 litres of any gas at NTP has a mass equal to its gram molecular weight and air contains 21 % oxygen by volume. Hence, the volume of air required can also be calculated.

Calculation of quantity of flue gases

The gases coming out after combustion $CO_{2,}$ SO_2, CO, O_2, N_2 are called flue gases. The water vapours formed condense as the gases cool down while the ash is excluded as it does not take part in combustion. Therefore, water vapours and ash are not included while calculating the percentage of dry combustion products.

Calculation of the flue gases when minimum amount of air is supplied

All the O_2 of air will be used in combustion of carbon and sulphur while N_2 in air remains unreacted. Let 1 kg of fuel contain C kg of carbon and S kg of sulphur. The weight of CO_2 and SO_2 thus formed in the combustion of fuel is calculated as follows

$$\underset{12\text{ kg}}{C} + O_2 \rightarrow \underset{44\text{ kg}}{CO_2}$$

12 kg of carbon on combustion gives 44 kg of carbon dioxide.

Therefore, C kg of carbon gives $\frac{44}{12} \times C$ kg of CO_2.

Similarly,

$$\underset{32\text{ kg}}{S} + O_2 \rightarrow \underset{64\text{ kg}}{SO_2}$$

32 kg of sulphur on combustion gives 64 kg of sulphur dioxide.

S kg of sulphur gives $\frac{64}{32} \times S$ kg or 2S kg of SO_2.

Weight of $N_2 = \frac{77}{100} \times$ weight of air supplied + weight of N_2 per kg of fuel.

Total weight of dry flue gases formed by the combustion of 1kg of fuel =

Weight of CO_2 + weight of SO_2 + weight of N_2

The % composition by weight of each constituent can then be calculated.

Calculation of the flue gases when excess of air is supplied

(i) CO_2 and SO_2 are calculated as mentioned above.

(ii) N_2 in flue gas = N_2 of total air supplied + N_2 present in the fuel.

(iii) When excess air is supplied the flue gas will contain O_2 of excess air.

Hence, the total weight of flue gas per kg of the fuel (when excess air is supplied)

= weight of CO_2 + weight of SO_2 + weight of N_2 + weight of O_2

Important facts for combustion calculation

(i) Substances always combine in definite proportion.

$$\underset{12\text{ g}}{C} + \underset{32\text{ g}}{O_2} \rightarrow \underset{44\text{ g}}{CO_2} + 97\text{ Kcal}$$

(ii)

Composition of air	% oxygen	% nitrogen
By volume	21	79
By weight	23	77

Thus, 1 kg of oxygen is supplied by $1 \times \frac{100}{23} = 4.35$ kg of air.

1 m^3 of oxygen is supplied by $1 \times \frac{100}{21} = 4.76$ m^3 of air.

(iii) The average molecular weight of air is taken as 28.94 g mol^{-1}

1 g mole of any gas at NTP (0°C and 760 mm pressure) occupies 22.4 *l*, i.e., weight of 22400 ml of a gas at NTP is its molecular mass.

(iv) The mass of any gas can be converted into its volume by the gas law

PV = nRT where *n* is the number of moles of the gas.

(v) Minimum oxygen required for combustion = theoretical oxygen required–O_2 present in fuel.

(vi) Combustion seldom takes place efficiently with minimum weight of oxygen or air. An excess of air has to be supplied for proper combustion.

$$\% \text{ Excess air} = \frac{\text{Actual air used} - \text{Minimum weight of air required}}{\text{Minimum weight of air required}} \times 100$$

(vii) Actual amount of air supplied is found out by taking excess air into consideration.

(ix) To convert weight into volume and vice versa the Avogadro's law is used.

(x) Let the weight of air required = *x* kg

According to Avogadro's law,

28.94 g air occupies 22.4 *l*

or, 28.94 kg of air occupies 22.4 m^3.

x kg of air occupies $\frac{22.4}{28.94} \times x$ m^3 volume

(Since, 1 m^3 = 1000 *l* and 1kg = 1000 g)

If minimum weight of air is used for combustion the dry flue gas will contain

$CO_2 + N_2$ of air + SO_2

(xi) If excess air is used is used for combustion then the dry flue gases will contain

$CO_2 + SO_2 + N_2$ of the total air supplied + O_2 from excess air.

Combustion of gaseous fuel

CO, H_2 and hydrocarbons such as CH_4, C_2H_6, etc are the main constituents of common gaseous fuels. The quantity of O_2 or air required in such cases is measured by the volume according to the combustion reactions of the constituents.

Combustion of carbon monoxide

$2CO + O_2 \rightarrow 2CO_2$

Thus, 2 volume of CO combine with 1 volume of O_2 to give 2 volume of CO_2

Combustion of H_2

$2H_2 + O_2 \rightarrow 2H_2O$

Here 2 volumes of H_2 combines with 1 volume of O_2

Combustion of CH_4

$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$
1 volume of methane reacts with 2 volumes of O_2

Similarly, other combustion reactions are

$$\begin{array}{llll} C_2H_6 & + \frac{7}{2}O_2 & \rightarrow 2CO_2 & + H_2O \\ \text{1 vol} & \text{3.5vol} & \text{2 vol} & \end{array}$$

$$\begin{array}{llll} C_2H_4 & + 3O_2 & \rightarrow 2CO_2 & + 2H_2O \\ \text{1 vol} & \text{3 vol} & \text{2 vol} & \end{array}$$

$$\begin{array}{llll} C_2H_2 & + 5/2\ O_2 & \rightarrow 2CO_2 & + 2H_2O \\ \text{1vol} & \text{2.5 vol} & \text{2 vol} & \end{array}$$

$$\begin{array}{llll} C_3H_8 & + 5O_2 & \rightarrow 3CO_2 & + 4H_2O \\ \text{1 vol} & \text{5 vol} & \text{3 vol} & \end{array}$$

The other constituents such as CO_2 and N_2 do not require any oxygen.

If the percentage composition of a gaseous fuel is known then the amount of O_2 required for combustion can be calculated with the help of the combustion equations. If the fuel already contains oxygen then that amount is subtracted from the total O_2 required. As air contains 21 % O_2 by volume, the volume of air required can be calculated by multiplying with 100/21.

To determine the percentage composition of dry flue gases the volume of CO_2 is also calculated as above. N_2 of the fuel comes out along with the flue gases; hence, the total N_2 in flue gases is N_2 in fuel + N_2 in air supplied for combustion. If excess air is supplied then the volume of O_2 present in the excess air is also taken into account. Percentage composition of dry flue gases is then calculated. Dry flue gases do not contain water vapour as they condense on cooling, hence, H_2O is not included in the calculation of the % composition of dry flue gases.

Problems Based on Weight Calculations

Solved Examples

1. Calculate the weight and volume of air required for the combustion of 3 Kg of carbon.

Solution

Combustion reaction

$$\underset{12\text{ g}}{C} + \underset{32\text{ g}}{O_2} \rightarrow CO_2$$

Weight of oxygen required to burn 12 kg C = 32 kg

Weight of oxygen required to burn 3 kg C = $\frac{32}{12} \times 3 = 8$ kg

As, air contains 23 % oxygen by weight

Therefore, weight of air required = $8 \times \frac{100}{23} = 34.783$ kg = 34783 g

Volume of air required

as, 1 mole of any gas at NTP occupies 22.4 L

Therefore, volume occupied by 1 mole air = 28.94 g air = 22.4 L

(molecular weight of air = 28.94 g)

Volume occupied by 34783 g of air = $\frac{22.4}{28.94} \times 34783$

$= 26.92 \times 10^3$ L $= 26.92$ m^3

(Since 1L = 10^3 m^3)

2. Calculate the mass of air needed for the complete combustion of 5 Kg of coal containing C = 80%; H = 15%, O = rest

Solution

Constituent	Amount per kg of the coal sample	Combustion reaction	Weight of O_2 required
C	0.80 kg	$C + O_2 \rightarrow CO_2$	$0.80 \times \frac{32}{12} = 2.133$ kg

H	0.15 kg	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.15 \times \frac{16}{2} = 1.20$ kg
O	1.00–(0.80 + 0.15) = 0.05 kg		
			Total O_2 required = 2.133 + 1.20=3.333 kg

Oxygen required from air = Total O_2 required – O_2 in fuel

$$= 3.333 - 0.05 = 3.283 \text{ Kg}$$

Weight of air required for combustion of 1 Kg of fuel = $3.283 \times \frac{100}{23} = 14.27$ Kg

Therefore, Weight of air required for combustion of 5 Kg of fuel = 14.27 × 5 = 71.369 kg

[Ans = 71.369 Kg]

3. A sample of coal was found to have the following composition by weight

C = 75%; H = 5.2%; O = 12.1%; N = 3.2% and ash = 4.5%

Calculate (i) minimum amount of O_2 and air necessary for complete combustion of 1 kg of coal; (ii) weight of air required if 40% excess air is supplied.

Solution

Constituent	**Amount per kg of the coal sample**	**Combustion reaction**	**Weight of O_2 required**
C	0.75 kg	$C + O_2 \rightarrow CO_2$	$0.75 \times \frac{32}{12} = 2$ kg
H	0.052 kg	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.052 \times \frac{16}{2} = 0.416$ kg
O	0.121 kg	–	–
N	0.032 kg	–	–
Ash	0.045 kg	–	–
		–	Total O_2 required = 2.416 kg

O_2 required from air = Total O_2 required – O_2 in fuel

= 2.416 kg – 0.121 kg = 2.295 kg

Minimum weight of air required = $2.295 \times \frac{100}{23}$ = 9.978 kg.

Weight of excess air = $9.978 \times \frac{40}{100}$ = 3.9912 kg

Total air supplied = 9.978 + 3.9912 = 13.969 kg.

[Ans = 13.969 kg]

4. A fuel is found to contain C = 90%; H = 6.0%; S = 2.5%; O = 1.0% and ash = 0.5 %. Calculate the amount of air required for complete combustion of 1 kg of fuel. If 25% excess air is used for combustion, calculate the percentage composition of the dry products of combustion.

Solution

Constituent	**Amount per kg of the coal sample**	**Combustion reaction**	**Weight of O_2 required**	**Weight of dry flue gas**
C	0.90 kg	$C + O_2 \rightarrow CO_2$	$0.90 \times \frac{32}{12} = 2.4$ kg	$0.90 \times \frac{44}{12} = 3.3$ kg
H	0.06 kg	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.06 \times \frac{16}{2} = 0.48$ kg	H_2O does not constitute dry flue gas
S	0.025 kg	$S + O_2 \rightarrow SO_2$	$0.025 \times \frac{32}{32} = 0.025$ kg	$0.025 \times \frac{64}{32} = 0.05$ kg
O	0.01 kg	–	–	–
Ash	0.005 kg	–	–	–
		–	Total O_2 required = 2.4 + 0.48 + 0.025 kg = 2.905 kg	

O_2 required from air = Total O_2 required – O_2 in fuel

= 2.905 -0.01 = 2.895 Kg

Minimum weight of air required for combustion $2.895 \times \frac{100}{23}$ =12.587 kg

According to the question 25 % excess air is supplied

$$\text{Excess air} = 12.587 \times \frac{25}{100} = 3.147 \text{ kg}$$

Total air supplied = 12.587 Kg + 3.147 kg

= 15.734 kg

(i) Calculation of dry products in the flue gases

The flue gases contains CO_2, SO_2, O_2 from excess air and N_2 from the total air supplied.

Weight of CO_2 = 3.3 kg

Weight of SO_2 = 0.05 kg

$$\text{Weight of } O_2 = 3.147 \times \frac{23}{100} = 0.724 \text{ kg}$$

$$\text{Weight of } N_2 = 15.734 \times \frac{77}{100} = 12.115 \text{ kg}$$

Total weight of flue gases = 3.3+0.05+0.724+12.115 = 16.189kg

Percentage composition of dry flue gases

$$\% \, CO_2 = \frac{3.3}{16.189} \times 100 = 20.38 \, \%$$

$$\% \, SO_2 = \frac{0.05}{16.189} \times 100 = 0.309\%$$

$$\% \, O_2 = \frac{0.724}{16.189} \times 100 = 4.47 \, \%$$

$$\% N_2 = \frac{12.115}{16.189} \times 100 = 74.835 \, \%$$

Practice problems

1. A fuel is found to contain C = 90%; H = 3.5 %; S = 0.5 %; H_2O = 1.0 %; N = 0.5 % and ash = rest. Calculate the minimum amount of air required for complete combustion of 1 Kg of fuel.

[Ans = 11.6739 Kg]

2. A sample of coal is found to contain : C = 81%; H = 5.0 %; S = 1 %; O = 8.0 %; N=1% and ash = 4 %.Calculate the amount of air required for complete combustion of 1 Kg of fuel. Also calculate the percentage composition by weight of the dry products of combustion. Oxygen in air is 23% by weight.

[Ans (i)10.826 kg; (ii) CO_2 = 26.22%; N_2 = 73.005%; SO_2 = 0.1765%].

3. A sample of coal was found to contain: C = 80%; H = 5.0 %; N= 2%; O = 1.0 % and remaining ash.
   1. Calculate the amount of air required for complete combustion of 1 Kg of coal sample.
   2. If 45 % excess air is supplied, estimate the percentage composition of the dry products of combustion.

[Ans Air = 10.9708 kg; % CO_2 = 17.976%; N_2= 75.067%; O_2 = 6.956%]

Problems based on volume calculations

Solved Problems

1. A gas used in internal combustion engine had the following composition by volume : H_2 = 45%;CH_4 = 36%; CO = 15%; N_2 = 4%. Find the volume of air required for the combustion of 1 m^3 of the gas.

Solution

Constituent	Amount in 1m^3 of the fuel	Combustion reaction	Volume of O_2 required(m^3)
H_2	0.45 m^3	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	45 ×0.5 =0.225
CH_4	0.36 m^3	$CH_4 + 2 O_2 \rightarrow CO_2 + 2H_2O$	0.36 × 2 = 0.72
CO	0.15 m^3	$CO + \frac{1}{2} O_2 \rightarrow CO_2$	0.15 × 0.5 = 0.075
N_2	0.04 m^3		
			Total = 1.020

Therefore volume of air required per m^3 of the gas = 1.020 $m^3 \times \frac{100}{21} = 4.857 m^3$

2. A given sample of petrol contains H = 15.4% and C = 84.6%. Calculate the minimum volume of O_2 required for the combustion of this sample.

Solution

Constituent	Amount in 1 kg of petrol	Combustion reaction	Weight of O_2 required(kg)
H	0.154 kg	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.154 \times \frac{16}{2} = 1.232$ kg
C	0.846 kg	$C + O_2 \rightarrow CO_2$	$0.846 \times \frac{32}{12} = 2.256$ kg
			Total O_2 reqd = 3.488 kg

Weight of O_2 required for combustion of 1 kg fuel = 3.488 kg = 3488 g.

Since 1 mole = 32 g of O_2 at NTP occupies 22.4 L

Therefore 3488 g of O_2 at NTP occupies = $\frac{22.4}{32} \times 3488 = 2441.6\ L = 2.441\ m^3$

(Since 1000L = $1m^3$)

3. A gaseous fuel has the following composition by volume – CH_4 = 20 %; CO = 10%; CO_2 = 5%; O_2 = 2%; C_2H_4 = 5%; C_3H_8 = 8%, rest N_2.Calculate the volume of air supplied per m^3 of fuel and the % composition of dry flue gases.

Solution

Constituents	**Volume in 1 m^3 of gas**	**Combustion Reaction**	**O_2 required (in m^3)**	**Volume of dry flue gases(m^3)**
CH_4	0.20 m^3	$CH_4 + 2\ O_2 \rightarrow CO_2 + 2H_2O$	$0.20 \times 2 = 0.40\ m^3$	$CO_2 = 0.20\times1 = 0.20\ m^3$
CO	0.10 m^3	$CO + \frac{1}{2}\ O_2 \rightarrow CO_2$	$0.10 \times \frac{1}{2} = 0.05\ m^3$	$CO_2 = 0.10 \times 1 = 0.10\ m^3$
CO_2	0.05 m^3	–	–	$CO_2 = 0.05\ m^3$
O_2	0.02 m^3	–	–	
C_2H_4	0.05 m^3	$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	$0.05 \times 3 = 0.15\ m^3$	$CO_2 = 0.05 \times 2 = 0.10\ m^3$
C_3H_8	0.08 m^3	$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	$0.08 \times 5 = 0.40\ m^3$	$CO_2 = 0.08 \times 3 = 0.24\ m^3$
N_2	0.50	–	–	$N_2 = 0.50 + \frac{79}{100} \times$ $4.67 = 4.19\ m^3$
			Total O_2 reqd = 1.0 m^3 O_2 in fuel = 0.020 m^3 Net O_2 reqd. = 0.98 m^3	

Volume of air required for the combustion of 1 m^3 of fuel = $0.98 \times \frac{100}{21} = 4.67\ m^3$

Calculation of dry flue gases

$CO_2 = (0.20+0.10+0.05+0.10+0.24)\ m^3 = 0.69\ m^3$

$N_2 = N_2$ (fuel) + N_2 (from air) = 4.19 m^3

Total volume of dry products = 0.69 +4.19 = 4.88 m^3

$$\%\ CO_2 = \frac{0.69}{4.88} \times 100 = 14.139\ \%$$

$$\%\ N_2 = \frac{4.19}{4.88} \times 100 = 85.861\ \%$$

4. A gaseous fuel has the following composition by volume – CH_4 = 4.0 %; CO = 26%; CO_2 = 10%; H_2 = 10%; N_2= 0.50%. If 20% excess air is supplied calculate the volume of air supplied and the % composition of dry flue gases.

Solution

Constituents	Volume in 1 m^3 of gas	Combustion Reaction	O_2 required (in m^3)	Volume of dry flue gases(m^3)
CH_4	0.04 m^3	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	0.04 × 2 = 0.08 m^3	CO_2 = 0.04 × 1 = 0.04 m^3
CO	0.26 m^3	$CO + \frac{1}{2} O_2 \rightarrow CO_2$	$0.26 \times \frac{1}{2} = 0.13$ m^3	CO_2 = 0.26 × 1 = 0.26 m^3
H_2	0.10 m^3	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.10 \times \frac{1}{2} = 0.05$ m^3	
CO_2	0.10 m^3	–	-	CO_2 = 0.10 m^3
N_2	0.50 m^3	–	-	0.50 m^3 + N_2 in total air supplied
			Volume of O_2 required = 0.260 m^3	Total CO_2 in flue gas = 0.40 m^3

$$\text{Minimum volume of air required} = 0.260 \times \frac{100}{21} = 1.238 \text{ m}^3$$

$$\text{Excess air} = 1.238 \times \frac{20}{100} = 0.2476 \text{ m}^3$$

Total air supplied = 1.238 m^3 + 0.2476 m^3 = 1.4856 m^3

Calculation of volume of dry flue gases

The flue gas contains CO_2, O_2 from excess air and N_2 of fuel + N_2 of total air supplied.

CO_2 = 0.40 m^3

$$O_2 = 0.2476 \times \frac{21}{100} = 0.052 \text{ m}^3$$

$$N_2 = 0.50 \text{ m}^3 \text{ (of fuel gas)} + 1.4856 \times \frac{79}{100} \text{ (from total air supplied)}$$

N_2 = 0.50 + 1.1174 = 1.674 m^3.

Total volume of dry flue gases = (0.40 + 0.052 + 1.674)m^3 = 2.126 m^3

$$\%\ CO_2 = \frac{0.40}{2.126} \times 100 = 18.81\ \%$$

$$\%O_2 = \frac{0.052}{2.126} \times 100 = 2.446\ \%$$

$$\%\ N_2 = \frac{1.674}{2.126} \times 100 = 78.74\ \%$$

Practice problems

1. Calculate the volume of air (volume % of oxygen in air = 21) required for the complete combustion of one 1L of CO.

[Ans = 2.381 L]

2. Calculate the volume of air required for the complete combustion of 1 m^3 of gaseous fuel having the composition CO = 46%; CH_4 = 10%; H_2 = 40%; C_2H_2 = 2.0%; N_2 =1.0% and remaining being $CO_{2.}$

[Ans = 3.238m^3]

3. A gaseous fuel has the following composition by volume – CH_4 = 6 %; CO = 22%; O_2 = 4%; CO_2 = 4%; H_2 = 20%; N_2= 44%. 20% excess air is used. Find the weight of air actually supplied per m^3 of this gas. Molecular weight of air = 28.97.

[Ans = 2143.107g]

4. A gaseous fuel has the following composition by volume : H_2 = 25 %; CH_4 = 30%; C_2H_6 = 11%; C_2H_4 = 4.5%; C_4H_8 = 2.5%; CO = 6.0%; CO_2 = 8%; O_2 = 2% and N_2 = 12%. Calculate the air fuel ratio and volumetric analysis of dry products of combustion if 40% excess air is used.

[Ans (i) 9.366:1 (ii) CO_2 = 8.415%; N_2 = 77.166%; O_2 =14.418%]

Summary

- Fuel is a combustible substance containing carbon as the major constituent. On proper combustion it gives large amount of heat.
- Fuel can be : (i) primary or natural (ii) secondary or derived.
- Primary fuels are found in nature as such e.g, wood, peat, coal, petroleum.
- Secondary fuels are derived from primary fuels. e.g., charcoal, coke, kerosene, coal gas, etc.
- On the basis of aggregation fuels are classified as solid fuels, liquid fuels and gaseous fuels.
- Solid fuels are wood, coal, charcoal, coke etc.
- Coal can be converted into coke by the process of carbonization.
- There are two types of carbonization of coal (i) Low-temperature carbonization (ii) high-temperature carbonization.
- Metallurgical coke can be obtained by two methods (i) Beehive Oven and (ii) Otto Hoffman's by product oven method.
- The quality of coal is analysed by two methods : Proximate Analysis and Ultimate Analysis

- Proximate Analysis is used to measure the amount of moisture, volatile matter, ash and fixed carbon in the coal sample.
- Ultimate or Elemental Analysis measures the amount of carbon, hydrogen, oxygen, nitrogen and sulphur in the coal sample.
- The amount of heat liberated on combustion of unit mass of a fuel is its calorific value.
- Calorific value of solid and non-volatile liquid fuels is measured with the help of a bomb calorimeter.
- Junkers Calorimeter and Boy's Calorimeter are used for the determination of calorific value of gaseous and volatile liquid fuels.
- Calorific value can be found out theoretically with the help of Dulong's formula.
- Higher or Gross Calorific Value of a fuel is the heat liberated when a unit mass/ volume of the fuel is burnt completely and the gaseous products are cooled to room temperature.
- Net or Lower Calorific Value is the heat liberated when a unit mass /volume of the gaseous fuel is burnt completely and the gaseous products are allowed to escape.
- Liquid fuels are petrol, kerosene, diesel, etc.
- All the above are obtained by the fractional distillation of petroleum or crude oil.
- Of all the fractions obtained the most sought after is gasoline. The higher molecular weight fractions can be converted to low molecular weight fractions (gasoline) by cracking.
- Cracking is of two types: (i) Thermal and (ii) Catalytic. Catalytic cracking can be fixed bed catalytic cracking or fluidized bed catalytic cracking.
- Gasoline can be synthesized by Polymerization, Alkylation, Fischer Tropsch Method, Bergius method.
- The ignition quality of gasoline is measured by octane number, which is a measure of its knocking property.
- Knocking is the rattling sound produced in internal combustion engine
- The quality of gasoline can be improved by reforming i.e., by bringing about structural modifications its antiknock characteristics can be improved.
- Tetraethyl lead (TEL) and diethyl telluride $(C_2H_5)_2Te$ are added to gasoline to improve its antiknock characteristics.
- The ignition quality of diesel engine fuels is measured in terms of Cetane Number.
- Gaseous fuels are coal gas, oil gas, etc.
- Coal gas is obtained as a byproduct of the destructive distillation of coal.
- Oil gas is obtained by the cracking of kerosene oil.

- The gases produced on combustion are called flue gases and can be analysed by the Orsat's apparatus.
- By combustion calculations the amount of air required by weight and volume can be estimated and conditions can be controlled during the combustion process.

Review Questions

1. Define fuel. What are the different types of fuels and how are they classified?
2. What is calorific value of a fuel? Define gross calorific value and net calorific value of a fuel and write down the relation between them.
3. What is calorific value. How can you measure the calorific value of a solid fuel with the help of a bomb calorimeter.
4. With the help of a well-labeled diagram explain the determination of calorific value of a gaseous or volatile liquid fuel using a Junkers gas calorimeter.
5. Enumerate the important characteristics of a good fuel.
6. What is proximate analysis of coal? Why is it called so and discuss its significance.
7. What are the different types of fuels. Compare solid, liquid and gaseous fuels?
8. What is the necessity and significance of elemental analysis of coal. How can you analyze coal with the help of ultimate analysis.
9. What is carbonization of coal. Discuss the process of carbonization of coal.
10. What is metallurgical coke. What are the requisites of good coke used for metallurgical purpose.
11. What is the difference between low temperature and high temperature carbonization of coal. Why is coke preferred to coal in metallurgical operations?
12. How can you manufacture metallurgical coke using a Beehive coke oven? What are the limitations of this process?
13. Describe the manufacture of metallurgical coke with the help of Otto Hofmann's Oven or byproduct oven method. What are its advantages over the beehive coke oven method?
14. What is petroleum? Discuss the various steps of processing of petroleum to obtain gasoline and other important fractions.
15. With the help of a neat labeled diagram describe the fractional distillation of crude petroleum and name the various products obtained.
16. What is cracking. Why is it important. Discuss the fixed bed catalytic cracking method to obtain gasoline from heavy oils. What are the limitations of the process?
17. Explain the fluidized bed catalytic cracking process for the manufacture of gasoline from heavy oils. What are the advantages of this process over the fixed bed catalytic cracking?

18. Differentiate between thermal cracking and catalytic cracking. What are the advantages of catalytic cracking over thermal cracking.
19. What is synthetic petrol. Explain the Fischer –Tropsch and Bergius process for the manufacture of the same?
20. What is knocking. How is it related to the chemical structure of the fuel. How can you reduce knocking in an internal combustion engine?
21. Explain the process of knocking in a Diesel Engine Fuel. Define octane rating and cetane number of a fuel. How can you increase the octane number of a fuel.
22. What is reforming. Explain how reforming improves the quality of gasoline. Also explain the process of reforming with the help of a well-labeled diagram.
23. What are gaseous fuels? What are the merits and demerits of gaseous fuels over solid and liquid fuels?
24. Describe the manufacture of producer gas with the help of a neat and labeled diagram.
25. With the help of a well-labeled diagram explain the manufacture of oil gas. What is its constitution and give the applications of oil gas.
26. Explain the manufacture of coke oven gas with the help of a well-labeled diagram.
27. How can flue gas be analysed with the help of Orsat flue gas apparatus. Discuss the significance of flue gas analysis.
28. Distinguish between the following
    (a) Proximate and ultimate analyses
    (b) Coal and Coke.
    (c) Coking coals and caking coals
    (d) Octane number and Cetane number
    (e) Thermal and catalytic cracking.

Multiple Choice Questions

1. A good fuel has
    (a) Moderate ignition temperature and high calorific value
    (b) High ignition temperature and high calorific value
    (c) Low ignition temperature and low calorific value
    (d) Low ignition temperature and high calorific value
2. The total quantity of heat liberated when a unit mass (or volume) of a fuel is burnt completely is called its
    (a) Heat value
    (b) Calorific value
    (c) Burning value
    (d) Combustion value
3. Calorific value of a solid or non-volatile liquid fuel is found with the help of
    (a) Junkers calorimeter
    (b) Bomb calorimeter
    (c) Boys calorimeter
    (d) Orsat apparatus

4. On the basis of its carbon contents and contents of moisture and volatile matter the best quality coal is
    (a) Peat
    (b) Lignite
    (c) Bituminous
    (d) Anthracite
5. Ultimate analysis of coal is used to determine
    (a) Percentage of carbon and hydrogen
    (b) Percentage of sulphur
    (c) Percentage of nitrogen
    (d) All of the above
6. The following can be estimated using the proximate analysis of coal
    (a) Percentage of moisture
    (b) Percentage of volatile matter
    (c) Percentage of ash
    (d) All of the above
7. Which of the following byeproducts is not recovered in the Otto Hoffman's byeproduct coke oven method
    (a) LPG
    (b) Benzene
    (c) Naphthalene
    (d) Ammoniacal liquor
8. The process of breaking bigger hydrocarbons into simpler low boiling point fractions is called
    (a) Reforming
    (b) Cracking
    (c) Refining
    (d) Knocking
9. Synthetic petrol can be obtained by
    (a) Polymerization
    (b) Fischer–Tropsch method
    (c) Bergius process
    (d) All of the above
10. The process of bringing structural modifications in straight run gasoline to improve its antiknock characteristics is termed as
    (a) Cracking
    (b) Refining
    (c) Reforming
    (d) Knocking
11. Junkers calorimeter is used to determine the calorific value of a
    (a) Gaseous fuel
    (b) Solid fuel
    (c) Liquid fuel
    (d) None of the above
12. The ignition characteristics of diesel are expressed in terms of
    (a) Octane number
    (b) Cetane number
    (c) Viscosity
    (d) Flash & fire point
13. The addition of TEL to gasoline
    (a) Increases the viscosity of gasoline
    (b) Increases the rate of combustion of gasoline
    (c) Increases the octane number of gasoline
    (d) Decreases the octane number of gasoline

14. Following compounds have been arbitrarily assigned an octane number of zero and hundred, respectively
    (a) n-heptane and isooctane
    (b) n- octane and isoheptane
    (c) Isooctane and n-heptane
    (d) n-hexadecane and 2- methylnaphthalene
15. The cetane number of high-speed diesel, medium-speed diesel and low speed diesel are nearly
    (a) 40,30,20 respectively
    (b) 45,35,25 respectively
    (c) 50,40,30 respectively
    (d) 25,15,5 respectively
16. Oil gas is obtained by the cracking of
    (a) Diesel oil
    (b) Petrol
    (c) Kerosene oil
    (d) Heavy oil
17. Producer gas is a mixture of
    (a) $CO + N_2$
    (b) $CO + H_2$
    (c) $CO + CO_2$
    (d) $CO + O_2$
18. The gas named as 'blue gas' is
    (a) Producer gas
    (b) Water gas
    (c) CNG
    (d) LPG
19. The gases analysed by Orsat flue gas apparatus are
    (a) SO_2, O_2, CO_2, H_2O vapours
    (b) Cl_2, N_2, O_2, SO_2
    (c) SO_2, CO_2, N_2, O_2
    (d) CO_2, O_2, CO and N_2
20. Arrange n-heptane, isooctane and naphthalene in increasing order of their knocking tendency
    (a) Naphthalene < isooctane < n-heptane
    (b) Isooctane < n-heptane < naphthalene
    (c) n-heptane < naphthalene < isooctane
    (d) Naphthalene < n-heptane < isooctane
21. The catalyst used for the cracking of heavy oil is
    (a) Ni or Sn oleate
    (b) $Al_2O_3 + ZrO_2$ + clay
    (c) Co+ Th + MgO + keiselguhr
    (d) Pt - Al_2O_3
22. Power alcohol is a mixture of
    (a) Petrol + ethyl alcohol
    (b) Diesel + ethyl alcohol
    (c) Petrol + methyl alcohol
    (d) Diesel + methyl alcohol
23. Which of the following is not a renewable source of energy
    (a) Solar energy
    (b) Wind energy
    (c) Petrol
    (d) Energy from hydrogen.
24. Coke is preferred to coal in metallurgical process because of
    (a) High strength and high porosity
    (b) Less sulphur content and low ash
    (c) Burns with a short flame
    (d) All of the above

25. The lowest boiling fraction of crude oil is
    (a) Petroleum ether
    (b) Kerosene oil
    (c) Diesel oil
    (d) Gasoline or petrol

Solutions

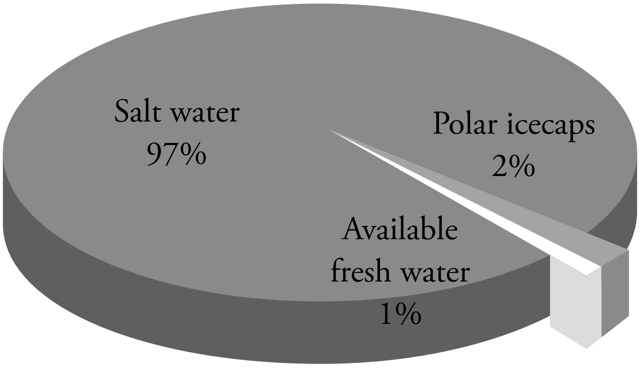
1 (a)
2 (b)
3 (b)
4 (d)
5 (d)
6 (d)
7 (a)
8 (b)
9 (d)
10 (c)
11 (a)
12 (b)
13 (c)
14 (a)
15 (b)
16 (c)
17 (a)
18 (b)
19 (d)
20 (a)
21 (b)
22 (a)
23 (c)
24 (d)
25 (a)

Chapter 2
WATER

2.1 Introduction

Water is the most precious, wonderful and useful gift of nature. It is the most abundant and essential natural resource. It covers nearly 70% of the earth's surface. It is estimated that the hydrosphere contains about 1360 million cubic km (1.3×10^{18} m^3) of water. Of this, about 97% is in the oceans and inland seas, which is not suitable for human consumption because of its high salt content. Of the remaining 3%, 2% is locked in the glaciers and polar ice caps and only 1% is available as fresh water in rivers, lakes, streams, reservoirs and ground water, which is suitable for human consumption.

Water on Earth



Source *www.aid-n.com/earths-water-resources-in-the world/earths water resources-water on earth published Nov 8, 2012.*

2.2 Sources of Water

The chief sources of water are

1. Surface water
2. Ground water
3. Rain water

(1) **Surface water sources** These include lakes, ponds, reservoirs, streams, rivers, seas and oceans.

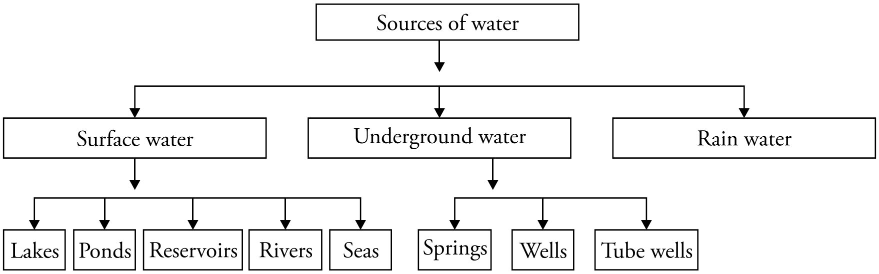
River water It contains dissolved minerals of the soils such as chlorides, sulphates, bicarbonates of sodium, calcium, magnesium and iron. It also contains organic matter derived from dead and decayed plants and animals; besides this, it contains sand and soil in suspension.

Water of lakes, pond and reservoirs They contain less of dissolved minerals but are rich in organic matter.

Sea water It is the most impure form of natural water. It contains on an average 3.5% of dissolved salts out of which about 2.6% is sodium chloride. Other salts present are sulphates of sodium, bicarbonates of potassium, magnesium and calcium, bromides of potassium and magnesium and a number of other compounds

(2) **Underground water sources** This is the water accumulated under the ground through seepage. It is obtained from wells, tube wells, springs, etc. Underground water is relatively free from suspended impurities because it is filtered as the water moves down through different layers of soil. The filtration also removes biological contamination. However, underground water is rich in dissolved salts.

(3) **Rain water** It is considered to be the purest form of water. However, it dissolves large amount of gases and suspended solid particles from the atmosphere. Rain water is divided between the two sources, a part of it seeps down to underground water tables and a part of it goes to the surface sources like rivers, ponds, lakes and reservoirs.



2.3 Effect of Water on Rocks and Minerals

Water brings about the weathering of rocks by various chemical processes like

(i) **Dissolution** Certain minerals and salts dissolve in water creating holes in the rock. This leads to the weakening of the rock that may ultimately lead to its collapse. Minerals like halite dissolve directly in water.

(ii) **Hydration** Under humid conditions and in the presence of moisture, the soil-forming minerals in the rocks swell leading to the increase in their volume. This further leads to the disintegration of the rocks in which these minerals are present. Some common examples are as follows

(a) $$\underset{\text{Anhydrite}}{CaSO_4 + 2\,H_2O} \xrightarrow{\text{Hydration}} \underset{\text{Gypsum}}{CaSO_4 .\ 2H_2O}$$

(b) $$\underset{\text{Bauxite}}{Al_2O_3 + 3H_2O} \xrightarrow{\text{Hydration}} \underset{\text{hydrated aluminium oxide}}{Al_2O_3 .\ 3H_2O}$$

(c) $$\underset{\text{Haematite (Red)}}{2Fe_2O_3 + 3H_2O} \xrightarrow{\text{Hydration}} \underset{\text{Limonite (yellow)}}{2Fe_2O_3 .\ 3H_2O}$$

(d) $$\underset{\text{Olivine}}{Mg_2SiO_4} \xrightarrow{\text{Hydration}} \underset{\text{serpentine}}{Mg_2SiO_4 .\ x\,H_2O}$$

(iii) **Hydrolysis** Water dissociates into H^+ and OH^- ions that combine with minerals to form new compounds. The silicates combine with water forming clays.

$$\underset{\text{(Orthoclase)}}{KAlSi_3O_8} + H_2O \rightarrow \underset{\text{(Acid silt clay)}}{HAlSi_3O_8} + KOH$$

The acid silt clay further recombines as

$$2HAlSi_3O_8 + 8H_2O \rightarrow \underset{\text{(Hydrated aluminium oxide)}}{Al_2O_3 .\ 3H_2O} + \underset{\text{(silicic acid)}}{6H_2SiO_3}$$

(vi) **Carbonation** Atmospheric carbondioxide dissolves in water to form carbonic acid.

$$H_2O + CO_2 \rightarrow H_2CO_3$$

This carbonic acid reacts with the rocks and minerals and dissolves them.

$$\underset{\text{Calcite}}{CaCO_3} + H_2O + CO_2 \rightarrow \underset{\text{Calcium bicarbonate (soluble)}}{Ca\,(HCO_3)_2}$$

The removal of $CaCO_3$ that holds the sand particles together leads to disintegration of rocks.

(v) **Oxidation** The oxygen present in soil water and atmosphere leads to oxidation and hydration

$$4FeO \text{ (ferrous oxide)} + O_2 \rightarrow 2Fe_2O_3 \text{ (ferric oxide)}$$

$$4Fe_3O_4 \text{ (magnetite)} + O_2 \xrightarrow{\text{oxidation}} 6Fe_2O_3 \text{ (haematite)}$$

$$2Fe_2O_3 \text{ (haematite)} + 3H_2O \xrightarrow{\text{Hydration}} 2Fe_2O_3 . 3H_2O \text{ (limonite)}$$

The affected rock becomes reddish brown because of oxidation. The rock weakens and crumbles easily.

2.4 Common Impurities of Water

Water is a very good solvent; therefore, it dissolves a large number of substances in it. The common impurities present in water are as follows

A. ***Dissolved impurities***

- These may be dissolved salts like carbonates, bicarbonates, nitrates, sulphates and chlorides of calcium, magnesium, sodium, potassium, iron, manganese, aluminium, etc.
- Dissolved gases like O_2, CO_2, SO_2, NH_3, N_2 and oxides of nitrogen also fall in this category.

B. ***Colloidal impurities*** These are those impurities whose particle size varies from 1 to 100 nm. It consists of finely divided silica, clay, aluminium hydroxide, ferric hydroxide, organic waste products, coloring matter, etc.

C. ***Suspended impurities*** These are impurities with particle size greater than 100 nm and can be removed by filtration or settling. They may be organic, inorganic or microorganism.

- ***Organic* impurities** consist of animal and vegetable matter, wood pieces, leaves, oil globules, etc.
- ***Inorganic impurities*** include clay, silica, sand, etc.
- ***Microorganisms*** include various types of algae, protozoa, bacteria and fungi.

Suspended impurities give turbidity and color to water. Microorganisms are the main cause of water-born diseases.

Characteristics imparted by impurities in water

Water is a very good solvent and dissolves various impurities in it. These substances present in water affect the characteristics of water in various ways. They alter the physical, chemical and biological characteristics of water. Let us discuss them one by one

Physical Characteristics

- Presence of salts like iron, manganese, industrial effluents, dyes from industries and other salts impart color to water.
- Presence of sand and silt make the water turbid.
- Salts also alter the taste of water. Presence of salts of sodium and potassium makes the water salty. Aluminium, manganese and iron make the water bitter. Presence of sodium bicarbonate gives soapy taste to water.
- Organic matter, decaying vegetation, algae, fungi and sewage impart a characteristic foul odor to water.

Chemical characteristics

Organic and inorganic chemicals like dyes, molasses, fertilizers, acids, alkalies, from industries insecticides, pesticides, liquors, wastes from tanneries, gases like NH_3, H_2S, etc, produced by anaerobic decomposition, etc, all these wastes alter the pH, alkalinity, acidity, hardness and chemical characteristics of water and make it unfit for domestic and industrial use.

Biological characteristics

The biological impurities like algae, fungi, pathogens and other microorganisms present in water either naturally or due to discharge of organic waste from domestic sewage, industrial houses or produced by the natural decay of organic matter all adversely affect the biological characteristics of water and make it unfit for domestic use, adversely affecting human health, aquatic flora and fauna.

Table 2.1 Common impurities in water and their effects

Type	Constituents	Effect
1. Suspended impurities	(a) Bacteria	Some causes diseases
	(b) Algae, protozoa	Odor, color, turbidity, diseases
	(c) Silts	Turbidity
2. Dissolved Impurities	(d) Salts	Alkalinity
	(i) Ca and Mg - bicarbonate	Alkalinity, hardness
	– Carbonates	Hardness
	–Sulphate	Hardness
	–Chloride	Hardness
	(ii) Na–bicarbonate	Alkalinity
	–Carbonate	Alkalinity
	–Sulphate	Foaming
	–Fluoride	Dental problems
	–Chloride	Affects taste
	(b) Metals and compounds	
	(i) Oxide of iron	Taste, color, corrosion, hardness
	(ii) Mn	Black and brown color
	(iii) Pb	Poisoning
	(iv) As	Poisoning
	(v) Ba	Effect on heart and nerves

	(vi) Cd	Illness
	(vii) CN	Fatal
	(viii) B	Nervous system
	(ix) Se	Highly toxic
	(x) Ag	Discoloration of skin, eyes
	(xi) Nitrates	Poisoning, color, blue baby syndrome
	(c) Vegetable dyes	acidity
	(d) Gases–Oxygen	Corrodes metals
	–Hydrogen sulphide	Odor, acidity, corrosiveness
	–Carbon dioxide	acidity, corrosion

2.5 Water Quality Standards

Importance of water quality standards

Water is widely used both in domestic and industrial life. Natural water, no matter how pure, contains some or the other impurities. Water quality standards are important because they help to identify the water quality, problems caused by improper treatment of waste water discharge, run off, addition of fertilizers, chemicals from agricultural areas and so on. The parameters for water quality are decided according to its use. Work in the area of water quality tends to be focused on whether water is treated for human consumption or environmental purpose. It is important to specify water quality standards for the purpose of safety of human beings, drinking characteristics and for the health of ecosystems.

Environmental water quality also called ambient water quality specifies the quality of water in water bodies like lakes, rivers and oceans. Ambient water quality standards vary significantly because of different environmental conditions, ecosystem and intended human uses.

The water quality parameters or characteristics for which analysis is carried out generally fall into three groups

1. Physical characteristics.
2. Chemical characteristics.
3. Biological characteristics.

(1) **Physical characteristics**

These are characteristics that respond to touch, taste, sight, etc. These include turbidity, temperature, odor, color and taste.

(a) ***Color*** Clean water should be colorless. The presence of color in water indicates the presence of various minerals, decomposed organic matter like leaves, roots, organic and inorganic wastes, wastes from textile mill, paper pulp industries, food-processing industries, domestic wastes, wastes from laundry, dyeing, dairy products, etc.

(b) ***Taste and odor*** Water should be odorless and should have a fairly good taste. There are no specific units to measure these parameters but generally decaying organic matter imparts odor and bad taste to water. The minimum odor that can be detected is called threshold odor number (TON). The value of TON is determined as follows

$$\text{TON} = \frac{\text{A} + \text{B}}{\text{A}}$$

A = Volume of sample in ml; B = Volume of distilled water (i.e., odor-free water in ml).

(c) ***Temperature*** It is an important water quality parameter. High temperature indicates thermal pollution and disturbs aquatic ecosystem by reducing the dissolved oxygen in water.

(d) ***Electrical conductivity*** It gives an idea about the dissolved solids in water. Greater the amount of dissolved solids, higher will be the conductivity. It can be measured easily with the help of conductivity meter. The average value of conductivity for potable water should be less than 2 μmho/cm (μS/cm).

(2) Chemical characteristics

Some important chemical characteristics are pH, hardness, alkalinity, total dissolved solids, chlorides, fluorides, sulphates, phosphates, nitrates, metal, etc.

(a) ***pH*** The pH of normal drinking water is 6.5–8.5. It can be measured with the help of pH meter using a combined electrode (a glass electrode and a calomel electrode as reference electrode). pH scale ranges from 0 to 14. pH 7 indicates neutral solution, less than 7 is acidic, whereas greater than 7 signifies alkaline or basic water.

(b) ***Hardness*** It expresses the concentration of calcium and magnesium ions in water in terms of equivalent of $CaCO_3$. The maximum acceptance limit is 500 ppm.

(c) ***Total dissolved solids (TDS)*** The maximum permissible limit is 500 mg/l. TDS includes both organic and inorganic dissolved impurities. It can be measured by evaporating a sample to dryness and then weighing the residue.

(d) ***Total solids*** This includes both the dissolved solids as well as suspended impurities.

(e) ***Dissolved oxygen*** It is an important water quality parameter. Higher the amount of DO better is the quality of water. Normal water contains 4.7 mg/l of DO. Lesser amount of DO in water indicates pollution in water. Wrinkler or iodometric methods using membrane electrode is used for measuring DO in water.

(f) ***Chlorides*** Its amount in water should be less than 250 ppm. High percentage of chloride in water harms metallic pipes as well as agriculture crops.

(g) **Fluorides** Maximum permissible limit is 1.5 ppm. The amount of fluoride in water sample can be determined using an ion meter. Excess of fluoride causes discoloration of teeth, bone fluorosis and skeletal abnormalities.

(h) ***Sulphates*** Permissible limit is 250 ppm. These are generally found associated with calcium, magnesium and sodium ions. It leads to scale formation in boilers, causes boiler corrosion and imparts odor to water.

(i) ***Nitrates*** Its concentration in drinking water should not exceed 45 mg/l. Excessive nitrates in drinking water causes ‘methemoglobinemia’ or blue baby syndrome in infants. Nitrates dissolve in water because of leaching of fertilizers from soil and nitrification of organic matter.

(3) **Biological characteristics**

Water should be free from all types of bacteria, viruses, protozoa and algae. The coliform count in any sample of 100 ml should be zero.

(4) **Bacteriological standards**

(i) ***Water entering the distribution system*** Coliform count in any sample of 100 ml should be zero. A sample of water entering the distribution system that does not confirm to this standard calls for an immediate investigation into both the efficacy of the purification process and the method of sampling.

(ii) ***Water in the distribution system*** Shall satisfy these three criteria

(a) *E. coli* count in 100 ml of any sample should be zero.

(b) Coliform organism should not be more than 10 per 100 ml of any sample.

(c) Coliform organism should not be present in 100 ml of any two consecutive samples or more than 5% of the samples collected for the year.

(5) ***Virological standards*** 0.5 mg/l of free residual chlorine for 1 h is sufficient to inactivate virus, even in water that was originally polluted. This free residual chlorine should be present in all disinfected supplies in area suspected of infectious hepatitis to inactivate virus and also bacteria. For water supply in such areas, 0.2 mg/l of free residual chlorine for half an hour should be insisted.

The Indian Standard for drinking water prescribed by the Bureau of Indian Standards and Indian Council of Medical Research are tabulated below.

Table 2.2 BIS 105000: Indian standard of drinking water specification

S.No	Substance or characteristic	Acceptable limit	Cause of rejection
	Essential characteristics		
1	Color (units on platinum – cobalt scale)	5	25
2	Odor	Unobjectionable	Unobjectionable
3	Taste	Agreeable	Agreeable
4	Turbidity (JTU, Max)	5	10
5	pH value	7.0–8.5	6.5–9.2
6	Total hardness (as $CaCO_3$) mg/l	200	600
7	Iron (as Fe in mg/l)	0.1	1.0
8	Chlorides (as Cl in mg/l)	200	1000
9	Residual, free chloride, mg/l	0.2	-
	Desirable characteristics		
10	Total dissolved solids mg/l	500	1500
11	Calcium (as Ca), mg/l	75	200
12	Copper (as Cu), mg/l	0.05	1.5
13	Manganese (as Mn), mg/l	0.05	0.5
14	Sulphate (as SO_4), mg/l	200	400
15	Nitrate (as NO_3), mg/l	45	45

16	Fluoride (as F), mg/l	1.0	1.5
17	Phenolic compounds (as C_6H_5OH), mg/l	0.001	0.002
18	Mercury (as Hg), in mg/l	0.001	No relaxation
19	Cadmium (as Cd), in mg/l	0.01	No relaxation
20	Selenium (as Se), in mg/l	0.01	No relaxation
21	Arsenic (as As), in mg/l	0.05	No relaxation
22	Cyanide (as CN), in mg/l	0.05	No relaxation
23	Lead (as Pb), in mg/l	0.1	No relaxation
24	Zinc (as Zn), in mg/l	5	15
25	Anionic detergents (as MBAS), in mg/l	0.2	1.0
26	Chromium (as Cr^{+6}), mg/l	0.05	No relaxation
27	Polynuclear aromatic hydrocarbons (as PAH), mg/l	0.2	0.2
28	Mineral oil, mg/l	0.01	0.3
29	Pesticides, mg/l	Absent	0.001
30	Radioactive materials (i) Gross alpha emitters pCi/l (ii) Gross beta emitters pCi/l	 3 30	 3 30
31	Alkalinity, mg/l	200	600
32	Aluminium (as Al), mg/l	0.03	0.2
33	Boron, mg/l	1	1

(Note: The values indicated under the column 'acceptable' are the limits upto which water is generally acceptable to consumers. Values in excess of those mentioned under 'acceptable' render the water not acceptable but still may be tolerated in the absence of alternative and better source upto the limits indicated under column 'cause of rejection' above which the supply will have to be rejected.)

2.6 Hardness of Water

Definition It is defined as the characteristic of water that prevents lathering of soap. Originally, it was defined as the soap-consuming capacity of water.

Causes Hardness is due to the presence of certain soluble salts of Ca and Mg in water. A sample of hard water, when treated with soap (sodium or potassium salts of higher fatty acids like oleic, palmitic or stearic acid), does not form lather or foam but forms a white precipitate or scum instead. This is because of the formation of insoluble salts of calcium and magnesium.

Chemical reactions involved are

$$\underset{\substack{\text{Soap (Sodium}\\ \text{stearate)}}}{2C_{17}H_{35}COONa} + \underset{\substack{\text{(from}\\ \text{hard water)}}}{CaCl_2} \rightarrow \underset{\substack{\text{Calcium stearate}\\ \text{(Insoluble)}}}{(C_{17}H_{35}COO)_2Ca} \downarrow + 2NaCl$$

$$\underset{\text{Soap}}{2C_{17}H_{35}COONa} + \underset{\substack{\text{(from}\\ \text{hard water)}}}{MgSO_4} \rightarrow \underset{\substack{\text{Magnesium stearate}\\ \text{(Insoluble)}}}{(C_{17}H_{35}COO)_2Mg \downarrow} + Na_2SO_4$$

Other salts of calcium and magnesium like $CaSO_4$, $Ca(NO_3)_2$, $MgCl_2$, etc, also react in a similar way forming insoluble precipitates of calcium and magnesium salts of higher fatty acids.

Table 2.3 Difference between hard and soft water

S.No	Hard water	Soft water
1	Water that does not form lather with soap but forms white precipitate	Water that produces lather or foam easily with soap is called 'soft water'
2	It contains soluble salts of calcium magnesium and other heavy metal ions like Al^{+3}, Fe^{+3}, and Mn^{+2} dissolved in it	It does not contain dissolved salts of calcium and magnesium
3	In hard water, the cleaning properties of soap is depressed and lot of soap is wasted in bathing and washing	The cleaning quality of soap is not depressed hence it is good for washing and cleaning
4	Owing to dissolved hardness, boiling point of water is elevated, therefore more fuel and time is required for cooking	Less fuel and time is required for cooking

Types of hardness

Hardness is of two types

1. Temporary hardness
2. Permanent hardness

(1) **Temporary hardness**

(a) It is also called carbonate hardness or alkaline hardness. It is called alkaline hardness because it is due to the presence of bicarbonate, carbonate and hydroxide and can be determined by titration with HCl using methyl orange as an indicator.

(b) It can be removed by boiling of water. During boiling, the bicarbonates are decomposed forming insoluble carbonates or hydroxides that are deposited at the bottom of the vessel.

$$\underset{\substack{\text{Calcium}\\ \text{bicarbonate}}}{Ca\,(HCO_3)_2} \xrightarrow{\text{boil}} \underset{\substack{\text{Calcium carb}\\ \text{-onate (Insoluble)}}}{CaCO_3 \downarrow} + H_2O + CO_2 \uparrow$$

$$\underset{\substack{\text{Magnesium}\\ \text{bicarbonate}}}{Mg\,(HCO_3)_2} \xrightarrow{\text{boil}} \underset{\substack{\text{Magnesium}\\ \text{hydroxide}}}{Mg(OH)_2 \downarrow} + H_2O + 2CO_2 \uparrow$$

(2) **Permanent hardness**

(a) It is also called non-carbonate or non-alkaline hardness.

(b) It is due to the presence of dissolved chlorides, sulphates and nitrates of calcium, magnesium, iron and other heavy metals.

(c) Salts mainly responsible for permanent hardness are

$CaCl_2$, $CaSO_4$, $MgCl_2$, $MgSO_4$, $Ca(NO_3)_2$, etc.

(d) It cannot be removed by simple boiling but can be removed by special chemical methods, like Lime–soda process, Zeolite method, etc.

Table 2.4 Comparison between temporary and permanent hardness

S.No	Temporary hardness	Permanent hardness
1	Also called carbonate hardness or alkaline hardness	Also called non-carbonate or non-alkaline hardness
2	It is due to the presence of bicarbonate, carbonate of Ca and Mg	It is due to the presence of dissolved chlorides, sulphates and nitrates of calcium, magnesium, iron and other heavy metals
3	It can be removed by boiling $Ca(HCO_3)_2 \xrightarrow{boil} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$ $Mg(HCO_3)_2 \xrightarrow{boil} Mg(OH)_2 \downarrow + H_2O + 2CO_2 \uparrow$	Cannot be removed by simple boiling but can be removed by specific chemical methods, like lime–soda process, zeolite method, etc

Degree of hardness

Hardness is always calculated in terms of equivalent of $CaCO_3$, although hardness is never present in the form of $CaCO_3$. There are two basic reasons for choosing $CaCO_3$ as standard

(i) Calculations become easy as its molecular weight is exactly 100 (and equivalent weight is exactly 50).

(ii) It is the most insoluble salt that can be precipitated in water treatment.

Calculation of equivalents of $CaCO_3$

To find out hardness in a given water sample, it is essential to convert hardness due to different salts ($CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$, $MgCl_2$, $MgSO_4$, etc) in terms of equivalent of $CaCO_3$. This can be done by the formula

$$\text{Equivalent of } CaCO_3 = \frac{(\text{Mass of hardness producing substance}) \times (\text{Chemical equivalent of } CaCO_3)}{(\text{Chemical equivalent of hardness producing substance})},$$

- Chemical equivalent of $CaCO_3$ is 50
- Chemical equivalent of Salt = $\frac{\text{Molecular weight}}{\text{Valency}}$
- Chemical equivalent of Acid= $\frac{\text{Molecular weight}}{\text{Basicity}}$

Basicity is the number of replaceable hydrogen ions in an acid.

- Chemical equivalent of Base = $\frac{\text{Molecular weight}}{\text{Acidity}}$

Acidity is the number of replaceable hydroxyl ions in a base.

The ratio = $\frac{\text{Chemical equivalent of } CaCO_3}{\text{Chemical equivalent of hardness producing substance}}$, is constant for a particular compound and is called multiplication factor.

Hence, Equivalent of $CaCO_3$ = mass of hardness producing substance × multiplication factor. The formula and multiplication factor for different salts are tabulated in table 2.5

Table 2.5 Formula and multiplication factor for different salts

Dissolved salt/ ion	Molar mass	Chemical equivalent	Multiplication Factor = $\frac{\text{Eq Wt of } CaCO_3}{\text{Eq Wt of hardness producing substance}}$
$Ca(HCO)_3$	162	162/2 = 81	$\frac{100/2}{162/2} = \frac{100}{162}$
$Mg(HCO)_3$	146	146/2 = 73	$\frac{100/2}{146/2} = \frac{100}{146}$
$CaSO_4$	136	136/2 = 68	$\frac{100/2}{136/2} = \frac{100}{136}$
$CaCl_2$	111	111/2 = 55.5	$\frac{100/2}{111/2} = \frac{100}{111}$
$MgSO_4$	120	120/2 = 60	$\frac{100/2}{120/2} = \frac{100}{120}$
$MgCl_2$	95	95/2 = 47.5	$\frac{100/2}{95/2} = \frac{100}{95}$
$CaCO_3$	100	100/2 = 50	$\frac{100/2}{100/2} = \frac{100}{100}$
$MgCO_3$	84	84/2 = 42	$\frac{100/2}{84/2} = \frac{100}{84}$
$Mg(NO_3)_2$	148	148/2 = 74	$\frac{100/2}{148/2} = \frac{100}{148}$
Ca^{++}	40	40/2 = 20	$\frac{100/2}{40/2} = \frac{100}{40}$
Mg^{++}	24	24/2 = 12	$\frac{100/2}{24/2} = \frac{100}{24}$

HCO_3^-	61	61/1 = 61	$\frac{100/2}{61/1} = \frac{100}{2\times 61} = \frac{100}{122}$
CO_3^{2-}	60	60/2 = 30	$\frac{100/2}{60/2} = \frac{100}{60}$
OH^-	17	17/1 = 17	$\frac{100/2}{17/1} = \frac{100}{2\times 17} = \frac{100}{34}$
H^+	1	1	$\frac{100/2}{1/1} = \frac{100}{2}$
CO_2	44	44/2 = 22	$\frac{100/2}{44/2} = \frac{100}{44}$
HCl	36.5	36.5/1 = 36.5	$\frac{100/2}{1\times 36.5} = \frac{100}{2\times 36.5} = \frac{100}{73}$
H_2SO_4	98	98/2 = 49	$\frac{100/2}{98/2} = \frac{100}{98}$
$FeSO_4 \cdot 7H_2O$	278	278/2 = 139	$\frac{100/2}{278/2} = \frac{100}{278}$
$Al_2(SO_4)_3$	342	342/6 = 57	$\frac{100/2}{342/6} = \frac{100\times 3}{342} = \frac{50}{57}$
$NaAlO_2$	82	82/1 = 82	$\frac{100/2}{82/1} = \frac{100}{82\times 2} = \frac{100}{164}$

Solved Examples

1. A water sample contains 248 mg $CaSO_4$ per litre. Calculate the hardness in terms of $CaCO_3$ equivalent.

Solution

Weight of $CaSO_4$ per litre = 248 mg

Hardness in terms of $CaCO_3$ equivalent = ?

$$\text{Equivalents of } CaCO_3 = \frac{[\text{Mass of hardness producing substance}]\times[\text{Chemical equivalent of } CaCO_3]}{\text{Chemical equivalent of hardness producing substance}}$$

$$\frac{248\times 100/2}{136/2} = 182.35 \text{ ppm.}$$